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DETERMINATION OF PREPOLYMER FUNCTIONALITY AND ITS RELATIONSHIP TO BINDER PROPERTIES

INTERIM TECHNICAL REPORT
FEBRUARY 3, 1969 - AUGUST 31, 1969

Prepared for

Air Force Rocket Propulsion Laboratory
Research and Technology Division
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Edwards, California

By

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Esso Research and Engineering Company
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Linden, New Jersey

Contract No. F04611-69-C-0046

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ESSO RESEARCH AND ENGINEERING COMPANY
GOVERNMENT RESEARCH LABORATORY
LINDEN, NEW JERSEY

FOREWORD

This report summarizes the results on the characterization of selected prepolymers with respect to functionality and functionality distribution carried out under Contract No. F04611-69-C-0046. These studies constitute a continuation of the work carried out under Contract No. F04611-67-C-0012, "Functionality Determination of Binder Prepolymers." The program consists of two phases. Phase I comprises the adaptation and application of analytical methods developed under Contract F04611-67-C-0012 to other prepolymers. It also provides direct service and support functions to existing solid propellant development programs. Phase II involves the scale-up of the fractionation procedure of prepolymers into pure difunctional and monofunctional components and a study of the effect of monofunctionality on the mechanical properties of the cured binder.

Specific studies relating to Shell's P-BEP prepolymer have already been published in a confidential report entitled "P-BEP Cure Studies," AFRPL-TR-69-179.

The program is sponsored by the Air Force Rocket Propulsion Laboratory, Research and Technology Division, Air Force Systems Command, Edwards, California and the program was administered by Captain Raymond Foscante and Dr. James Trout. The work reported was done in the Government Research Laboratory of the Esso Research and Engineering Company, Linden, New Jersey.

Research was carried out by Mr. A. H. Muenker with analytical support by Dr. B. E. Hudson. The project is under the supervision of Dr. D. Grafstein, Program Manager.

W. H. Ebelke, Colonel, USAF
Chief, Propellant Division

ABSTRACT

Functionality and functionality distribution measurements have been carried out on six different polybutadiene prepolymers containing hydroxy or carboxy functionality which are currently of interest to the Air Force. The specific prepolymers are: Sinclair's Poly B-D R-45M and R-15M, hydroxy-functional butadiene homopolymers prepared by free radical polymerization and General Tire's Telagen prepolymer series, prepared by anionic polymerization. The Telagen prepolymer series comprises the following polymers: the OH-Telagen (nominal Mn=5000) and its low molecular weight (Mn=2000), saturated counterpart, OH-Telagen-S, and the corresponding carboxy-functional analogues, COOH-Telagen and COOH-Telagen-S.

Number average molecular weight measurements of three different lots of the R-45M prepolymer showed little batch to batch variation. Functionality distribution measurements were obtained by elution chromatography on activated silica gel. The difunctional content was found to be approximately 40 wt % with a nominal molecular weight of 4000, the remainder (60 wt %) being trifunctional with a nominal molecular weight of 2000. All three lots of the R-45M have consistently shown this dependence of functionality on molecular weight. On a molar basis the functionality distribution of the R-45M prepolymer reflects an even high triol content: 25 mole % diol and 75 mole % triol. The functionality distribution of the R-15M was found to be similar to that of the R-45M, containing more than 50 wt % triol. In contrast to Sinclair's R-45M and R-15M prepolymers which are composed of di- and trifunctional components, the Telagen prepolymers contain non-, mono- and difunctional prepolymers. The total non- and monofunctional content of the four Telagen prepolymers which were analyzed varied from 24 to 32 wt %, the bulk of which is monofunctional.

TABLE OF CONTENTS

LISTING OF FIGURES

LISTING OF FIGURES (Cont'd)

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I. INTRODUCTION

Under Contract F04611-67-C-0012, Esso Research and Engineering Company developed and/or refined and evaluated test methods for determining molecular weight, equivalent weight, functionality, functionality distribution and molecular weight distribution of selected solid propellant binder prepolymers.

Most significantly a method was developed which can determine the functionality distribution of binder prepolymers. The method is based on the adsorption of prepolymer on activated silica gel and subsequent selective desorption by stepwise elution using solvent mixtures of progressively greater elution power. This technique can effectively separate prepolymers into non-, mono-, di- and polyfunctional components.

The ability to determine the functionality distribution of prepolymers and to separate prepolymers into non-, mono- and difunctional prepolymers is a prerequisite in studying the effect of functionality distribution on binder and propellant mechanical properties. It opens up new areas of binder studies such as the establishment of the relationship between mechanical properties and monofunctional prepolymer content. Such experimental investigations were hitherto inaccessible because of lack of appropriate analytical techniques.

Theoretical considerations predict that monofunctional prepolymer components will seriously affect the mechanical properties of the propellant since monofunctional polymer chains will act as chain terminators during the cure process and hence interfere with the formation of a large polymer network needed to impart good mechanical properties to the propellant. The level of monofunctional polymer at which mechanical properties will seriously drop off has not been defined and good quantitative data are needed. The question whether the presence of monofunctional polymer components can be off-set by the use of larger amounts of trifunctional curatives also needs to be resolved. A study of the effect of nonfunctional polymer components on cured binder properties is not anticipated. Nonfunctional prepolymer components cannot participate in the cure process and will therefore merely act as high molecular weight plasticizers.

Prepolymer composition particularly with respect to functionality distribution has long been neglected as a quality parameter in the optimization of solid propellant mechanical properties. Phase II of this program represents an initial step designed to fill this gap. It will attempt to establish a relationship between functionality, specifically monofunctional prepolymer content, and binder mechanical properties. It will also establish the optimum mechanical properties of a purely difunctional polybutadiene prepolymer. All studies under this program will be restricted to the gumstock. No total propellant formulation studies are planned.

II. OBJECTIVE

The objective of this program is to continue the development of methods for the characterization of selected prepolymers with respect to functionality and functionality distribution and to determine the relationship between gumstock mechanical properties and functionality, specifically monofunctional prepolymer content.

The program consists of two phases:

Phase I entails research aimed at extending and adapting analytical methods developed under Contract F04611-67-C-0012 to new classes of prepolymers of interest to the Air Force.

Phase II involves in part optimization and scale-up of the fractionation procedure to obtain larger quantities of pure difunctional and monofunctional prepolymers. Gumstock formulations employing pure difunctional polymer exclusively and with varying amounts of monofunctional material will be made to assess the general effect of functionality distribution on mechanical properties. In addition, gumstock formulations utilizing pure difunctional material will be compared with those employing the bulk polymer.

III. SUMMARY

This report discusses functionality and functionality distribution measurements of binder prepolymers currently of interest to the Air Force. This is the second interim report on Contract No. F04611-69-C-0046 and covers the period February 3, 1969 through August 31, 1969. All studies relating to Shell's P-BEP prepolymer have been summarized in AFRPL-TR-69-179, entitled "P-BEP Cure Studies."

A total of six different prepolymers were characterized with respect to functionality and functionality distribution. All are low molecular weight, liquid polybutadienes containing hydroxy or carboxy functionality.

Sinclair produces two hydroxy-functional butadiene homopolymers which are designated Poly B-D R-45M and R-15M respectively. The R-15M prepolymer has a somewhat higher molecular weight than the R-45M. Interest in these prepolymers stems from two facts: (1) their low cost (48 to 54 cents/pound) and their reportedly high overall functionality which is substantially in excess of 2.0.

Molecular weight and functionality as well as functionality distribution measurements were carried out on three different lots of the R-45M prepolymer to determine whether there were significant differences in these parameters, in particular in the functionality distribution pattern.

The extrapolated number average molecular weights, $(\bar{M}n)o$, as determined by VPO in chloroform at 37° showed very little batch to batch variation (2740 to 2900). The overall functionalities based on molecular weight and equivalent weight measurements varied from 2.30 to 2.48. In view of this high average functionality level, the R-45M prepolymer should contain significant quantities of polymer components having functionality greater than two. Subsequent functionality distribution measurements have confirmed this. Functionality distribution measurements were obtained by elution chromatography on activated silica gel (100-200 mesh). A comparison of functionality distribution measurements of three lots of the R-45M shows that this prepolymer consists of di- and trifunctional components. The difunctional content is approximately 40 wt %, with a nominal molecular weight of 4000, the remainder (60%) being trifunctional with a nominal molecular weight of 2000. All three lots have consistently shown this dependence of functionality on molecular weight. On a molar basis the functionality distribution of the R-45M prepolymer reflects an even higher triol content: 25 mole % diol and 75 mole % triol.

To determine whether there is a substantial difference between the R-45M and the R-15M prepolymer, a single lot of R-15M was also characterized with respect to its functionality and functionality distribution. Molecular weight measurements showed that there is a significant but not dramatic difference in molecular weight between the R-15M (Mn=3400) and the R-45M (Mn=2800). The overall functionality of the R-15M, lot 707203 was found to be 2.48 which is identical to lot 805101 of the R-45M

prepolymer. Functionality distribution measurements of the R-15M showed that about 45 wt % of this prepolymer is difunctional with a nominal molecular weight of 6000, the remainder being trifunctional.

A comparison of the functionality distribution of the R-45M and the R-15M prepolymers therefore shows that trifunctional prepolymer is the major component (more than 50 wt %) in both prepolymers. The R-15M appears to have a slightly higher difunctional content than the R-45M. This apparently slight difference in difunctional polymer content may further diminish upon analysis of additional lots of the R-15M prepolymer.

Samples of General Tire's low molecular weight (nominal Mn=2000), hydrogenated OH-Telagen-S had previously been characterized and found to contain non-, mono- and difunctional prepolymer. One additional lot of OH-Telagen-S which is being used on Contract No. F04611-68-C-0045, "Synthesis and Evaluation of Curing Agents," has been analyzed. The functionality distribution of lot 242 AM 273 BH of OH-Telagen-S was found to be as follows: 9% nonfunctional, 15% monofunctional, the remainder being difunctional. Similar functionality distributions were found for previously analyzed lots of OH-Telagen-S.

A sample of the higher molecular weight (nominal Mn=5000), unsaturated OH-Telagen, has also been analyzed. This polymer is the first unsaturated, hydroxy functional prepolymer of the Telagen series of 5000 nominal molecular weight that we have tried to fractionate by functionality. The total non- and monofunctional content of lot 242 AM 292/316 AM6 was found to be about 32 wt %. Fractionation of this prepolymer will be scaled-up to provide sufficient quantities of pure difunctional material for evaluation of mechanical properties of cured gumstocks. Preliminary data suggest that separation can be achieved even at a silica gel/polymer ratio of 10/1 if the desorbing power of the eluting solvent is adjusted.

Functionality distribution measurements were also carried out on the carboxy-analogue of the OH-Telagen prepolymer series. The COOH-Telagen-S, lot 242 AM 273 CHR, a hydrogenated polybutadiene of 2000 nominal molecular weight was found to contain about 2 wt % nonfunctional and 23 wt % monofunctional prepolymer. This confirms our previous observations that the bulk of the material having less than theoretical functionality (f=2.0) is monofunctional (f=1) rather than nonfunctional (f=0).

The higher molecular weight (nominal Mn=5000), unsaturated COOH-Telagen prepolymer was found to be more strongly adsorbed on the silica gel than any of the previously characterized prepolymers. Polymer recovery upon fractionation on silica gel was only 51 to 69%. Nevertheless, the non- and monofunctional prepolymer components which are less strongly adsorbed on the silica gel were eluted from the column. The total non- and monofunctional content was found to be about 27%.

IV. TECHNICAL PROGRESS

A total of six different prepolymers were characterized with respect to functionality and functionality distribution. All are low molecular weight, liquid polybutadienes. They differ, however, in several respects:

- Different methods of polymerization are employed. The Telagen series, manufactured by General Tire and Rubber Company, uses an anionic polymerization process, whereas Sinclair's Poly B-D prepolymers are prepared by a free radical process. This difference in the method of polymerization results in:

  a. different microstructures and

  b. most significantly in different functionality distributions.

- The anionic process permits some control over the degree of 1,4 and 1,2-addition. The free radical process, however, gives consistently 80% 1,4-addition (60% trans-1,4 and 20% cis-1,4) and 20% 1,2-addition (vinyl groups). This difference in microstructure, however, is not explored on this program. Our objective was to quantitatively determine the functionality distribution of these prepolymers, a parameter which is of particular importance from the standpoint of mechanical properties of the cured gumstock.

- The Telagen prepolymer series is generally composed of non,-mono- and difunctional prepolymer, whereas the Sinclair Poly B-D series comprises di- and trifunctional components.

In addition to this difference in microstructure and functionality distribution, the following differences are reflected by these prepolymers:

- The type of functional group (OH vs COOH)

- Saturated (hydrogenated) vs unsaturated prepolymer (Telagen vs Telagen-S)

- There are also some differences in the molecular weights of these prepolymers.

The saturated Telagen has a lower molecular weight (nominal 2000) than the unsaturated Telagen (nominal 5000). The choice of a lower molecular weight, saturated prepolymer reflects the increased viscosity of the saturated backbone.

In the following sections, the results of functionality and functionality distribution measurements on six prepolymers are summarized.

A. Functionality and Functionality Distribution Measurements of Sinclair's POLY B-D Prepolymers

Sinclair's Poly B-D prepolymer series are low molecular weight, liquid butadiene homopolymers or copolymers of butadiene and styrene or acrylonitrile. The two hydroxy-functional homopolymers which are of interest as propellant binders are designated R-45M and R-15M. The R-15M has a somewhat higher molecular weight than the R-45M. The current price per pound (in drum quantities) is 48¢ for the R-15M and 54¢ for the R-45M. These prepolymers have consistently been reported to have overall functionalities substantially in excess of 2.0. In the following sections functionality and functionality distribution measurements of different polymer batches are discussed.

1. Sinclair's R-45M

Three different lots (704211, 805101 and 805201) of the R-45M prepolymer have been characterized with respect to functionality and functionality distribution.

1.1. Functionality Determination

Functionalities were calculated from number average molecular weight measurements and equivalent weight measurements:

$$f = \frac{\text{Number Average Molecular Weight}}{\text{Equivalent Weight}}$$

Number average molecular weights were obtained by VPO in chloroform at 37°C. All measurements were extrapolated to zero concentration to obtain $(\overline{Mn})o$. The concentration dependence of molecular weight for the three lots of R-45M are shown in Figures 1 through 3. They show a significant negative concentration dependence, the apparent molecular weight increasing with decrease in polymer concentration. The extrapolated molecular weights are summarized in Table I.

TABLE I

SUMMARY OF FUNCTIONALITY MEASUREMENTS OF THREE LOTS OF R-45M

Lot No.	$(\overline{Mn})o$	Equivalent Weight (Grams of Polymer/Mole of OH)	Functionality
740211	2740	1190	2.30
805101	2800	1130	2.48
805201	2900	1220	2.38

The equivalent weights were determined by reacting the polymer with p-toluenesulfonyl isocyanate in dilute chloroform solution. The reaction is monitored by infrared. Details of this analytical method have been described in AFRPL-TR-68-237 (1). The results of the equivalent

(1) Functionality Determination of Binder Prepolymers, Final Report, October 66-September 68, A. H. Muenker and B. E. Hudson, Esso Research and Engineering Co.

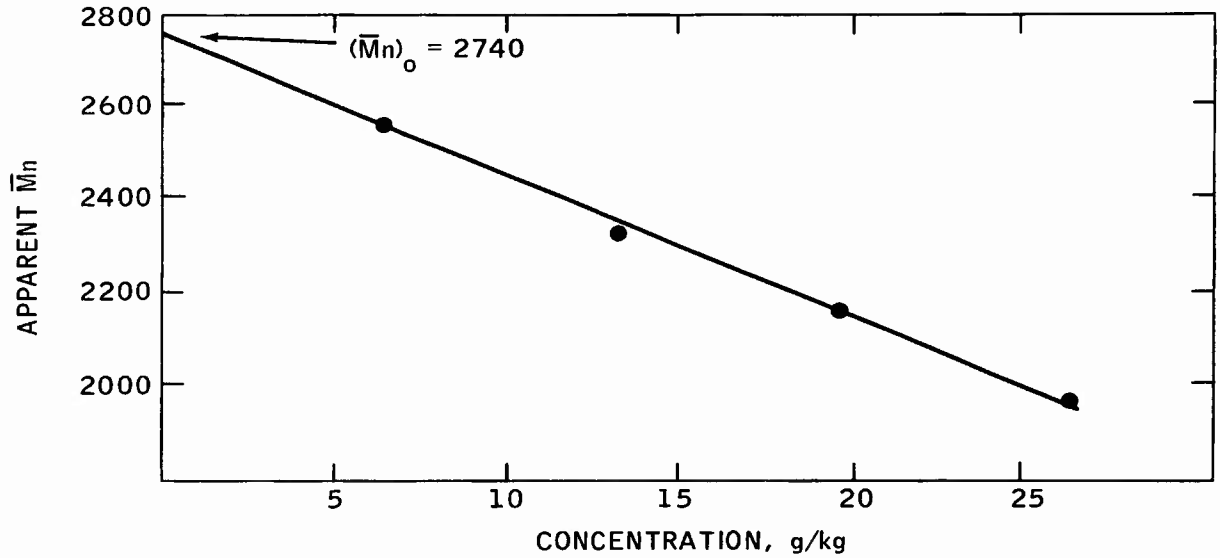

Figure 1. Concentration dependence of number average molecular weight for Poly B-D, R-45M, lot 704211, in chloroform at 37°C by VPO.

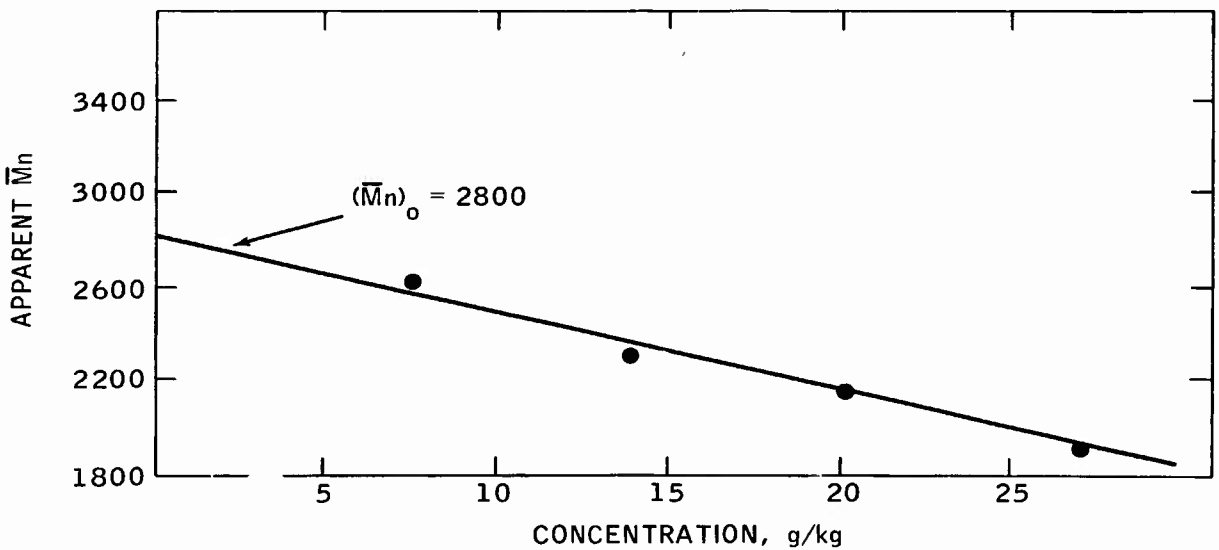

Figure 2. Concentration dependence of number average molecular weight for Poly B-D, R-45M, lot 805101, in chloroform at 37°C by VPO.

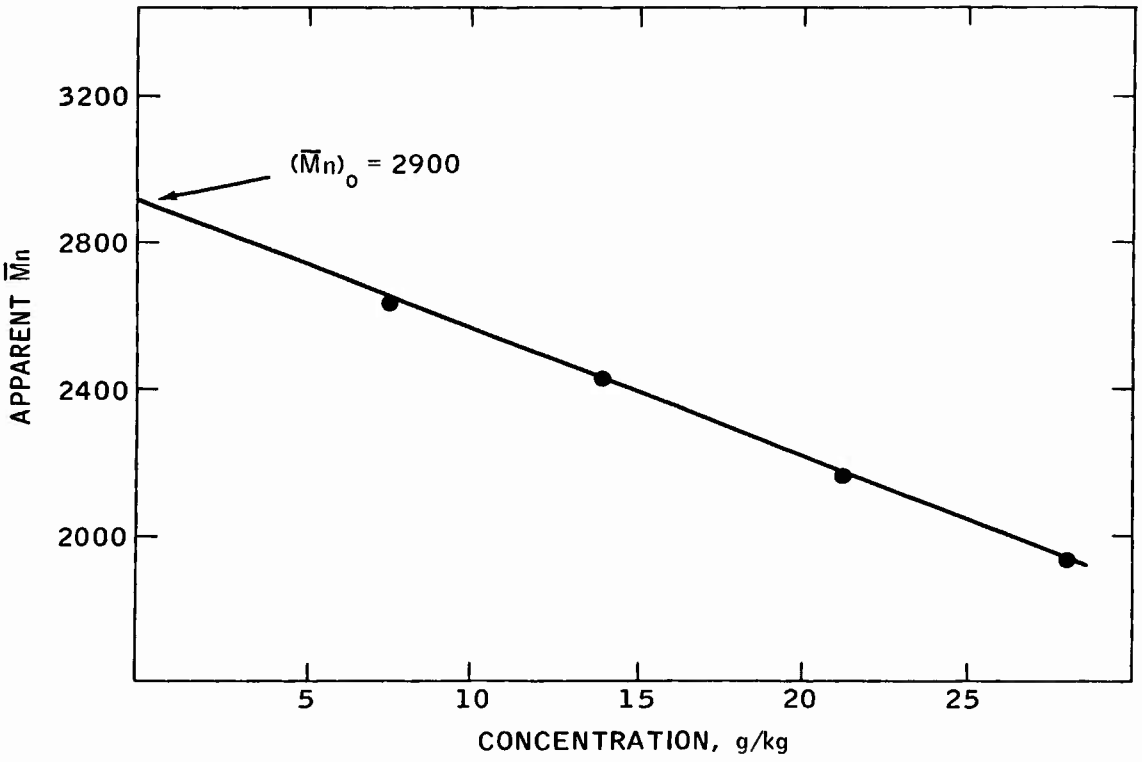

Figure 3. Concentration dependence of number average molecular weight for Poly B-D, R-45M lot 805201, in chloroform at 37°C by VPO.

weight measurements and the functionalities based on molecular weight and equivalent weight measurements are summarized in Table I.

These functionalities for three lots of R-45M are substantially in excess of 2.0. In view of this high average functionality (2.30 to 2.48) the R-45M prepolymer should contain significant quantities of polymer components having functionalities greater than two. Subsequent functionality distribution measurements have confirmed this.

1.2. Functionality Distribution Measurements

Functionality distribution measurements were made on all three lots to determine whether there were significant differences in the distribution pattern. We had previously demonstrated (1) that the R-45M contains no measureable quantities of non- and monofunctional prepolymer components. Our objective was therefore to separate the prepolymer into pure difunctional and polyfunctional components.

a. Lot 704211

The solvent schedule that was found to be particularly effective in separating R-45M by functionality was 100% CH_2Cl_2 followed by solvent mixtures of CH_2Cl_2 and CH_3CN.

Methylene chloride was used as the initial solvent instead of carbon tetrachloride which we have generally used for other prepolymers. Methylene chloride affords greater ease of desorption of the prepolymer. As shown in Figure 4, a fraction accounting for 42% was immediately eluted in response to methylene chloride. Based on the shape of the elution profile we recombined the individual cuts into four major fractions for subsequent analysis. The concentration dependence of molecular weight of the four fractions is shown in Figure 5. Analyses of these fractions are summarized below:

Identification: 447-64
Silica gel/polymer ratio: 87/1
Polymer charged to column: 1.15/g
Total polymer recovery: 95.0

Fraction	Wt % of Total	Equivalent Weight (Grams/mole of OH)	$(\bar{M}n)o$	Functionality
I	42.2	1930	4000	2.07
II	19.1	790	2400	3.04
III	25.4	730	2150	2.95
IV	8.3	530	1760	3.32
	95.0%			

Functionality data on the individual fractions show that fractionation by functionality has taken place. The prepolymer is clearly composed of di- and trifunctional polymer. About 42 wt % is difunctional, at least 45% is trifunctional, the remainder being trifunctional or tetrafunctional.

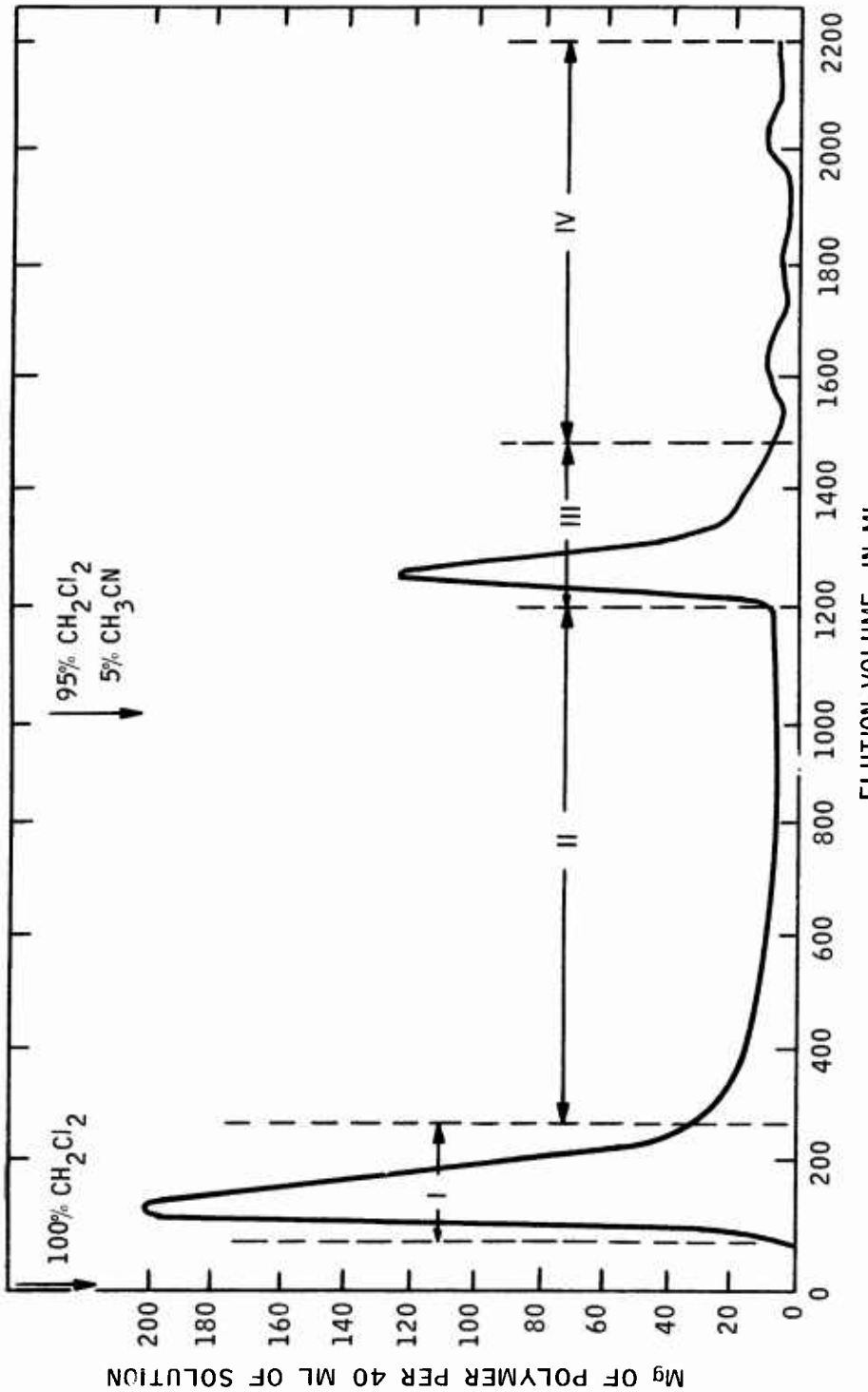

Figure 4. Elution Profile for Poly B-D, R-45M, lot 704211. Stepwise elution from silica gel.

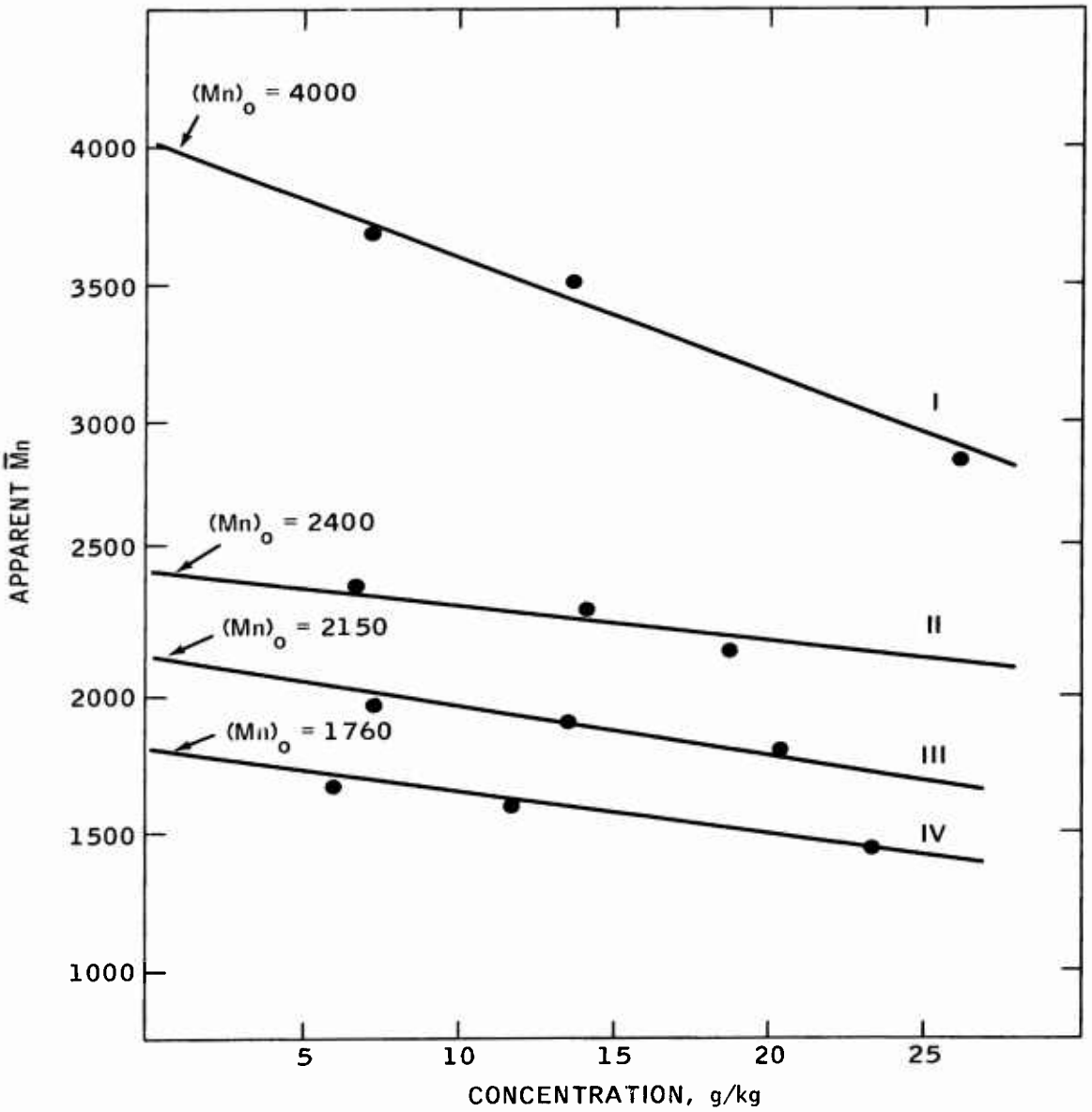

Figure 5. Concentration dependence of number average molecular weight for fractions I through IV of Sinclair's R-45M, lot 704211. Measurements were made by VPO in chloroform at 37°C.

Analysis of Fraction IV has raised the possibility that this prepolymer contains tetrafunctional components. The interesting finding is that functionality is a function of molecular weight, the low molecular weight components being trifunctional and the higher molecular weight fraction being difunctional.

Lots 805101 and 805201 were subsequently fractionated to determine the variation in functionality distribution among different batches.

b. Lot 805101

The solvent schedule was similar to that used for lot 704211 (100% CH_2Cl_2 followed by a solvent mixture of 95% CH_2Cl_2 and 5% CH_3CN). However, the profile was shortened by switching to the 95/5 CH_2Cl_2/CH_3CN mixture earlier in the elution schedule.

The resulting elution profile is shown in Figure 6. The individual cuts were recombined into four major fractions. During the recombination of Fractions I and II and subsequent stripping at 40°C we observed that these polymer fractions became insoluble. Apparently, oxidative crosslinking took place making the polymer insoluble. Therefore, no analyses could be obtained on Fractions I and II. Fractions III and IV did not show evidence of crosslinking and were therefore analyzed. Analyses of these fractions are summarized below:

Identification: 447-82
Silica gel/polymer ratio: 100/1
Polymer charged to column: 1.18 g
Total polymer recovery: 95.4%

Fraction	Wt % of Total	Equivalent Weight (Grams/mole of OH)	$(\overline{Mn})_o$	Functionality
I	37.2	---------- *		----------
II	10.0	---------- *		----------
III	37.9	860	2600	3.02
IV	10.3	570	1780	3.12
	95.4%			

*Samples had become insoluble due to oxidative crosslinking.

Analyses of Fractions III and IV showed that these fractions are trifunctional. Based on functionality distribution measurements of the previous lot of R-45M (lot 740211) and the similarity between the two profiles it can be assumed that Fraction I is difunctional and Fraction II is trifunctional. We therefore assign the following functionality distribution to lot 805101:

- 37% difunctinal
- 58% trifunctional
- remainder (5%) trifunctional or above

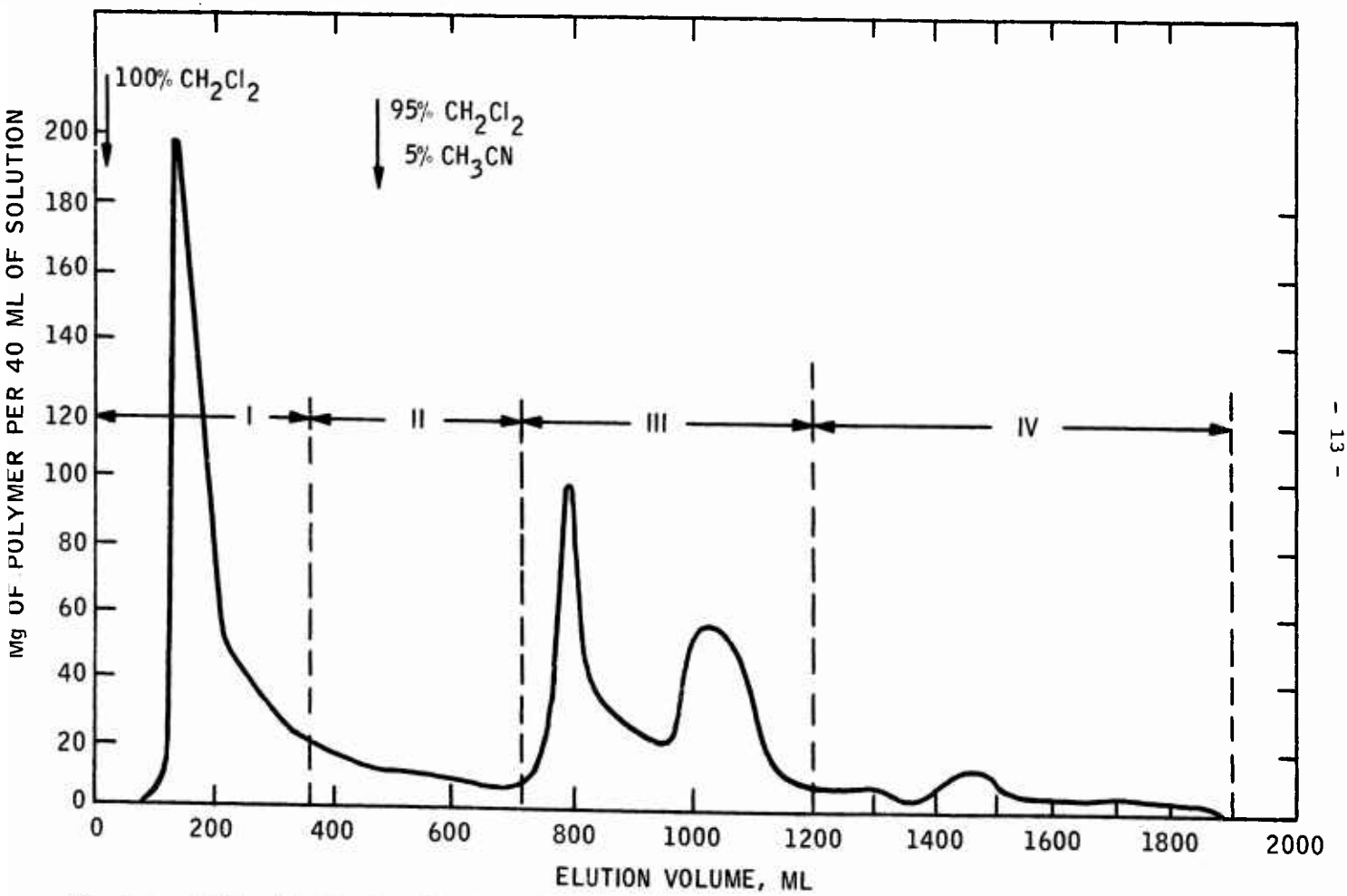

Figure 5. Elution Profile for Poly B-D, R-45M, lot 805101; stepwise elution from silica gel.

c. Lot 805201

The solvent schedule was again the same employed for lots 704211 and 805101 except for increasing the CH_3CN content to 20%. Increasing the CH_3CN solvent content did not, however, speed up the elution of the trifunctional polymer. The elution profile is shown in Figure 7. The individual cuts were recombined into three major fractions. Oxidative crosslinking again prevented the analysis of Fraction II. Based on elution profiles of previously analyzed R-45M samples this fraction is believed to be trifunctional. Analyses are summarized below:

Identification: 447-108
Silica gel/polymer ratio: 100/1
Polymer charged to column: 1.20 g
Total polymer recovery: 92.8%

Fraction	Wt % of Total	Equivalent Weight (Grams/mole of OH)	$\overline{(Mn)}o$	Functionality
I	43.0	2005	4100	2.04
II	7.4	---------- * ----------		
III	42.4	720	2100	2.92
	92.8%			

*Sample had become insoluble due to oxidative crosslinking before analyses could be obtained.

Lot 805201 therefore contains approximately 43% difunctional polymer of (Mn)o=4100, the remainder being trifunctional, having a molecular weight of about 2100.

A comparison of functionality distribution measurements of three lots of R-45M shows that the difunctional content is approximately 40%, with a nominal molecular weight of 4000, the remainder being trifunctional with a nominal molecular weight of 2000. All three lots have consistently shown this dependence of functionality on molecular weight.

On a molar basis, the functionality distribution of the R-45M prepolymer reflects an even higher triol content:

Functionality Distribution of R-45M on a Molar Basis:

Diol: 25 Mole %

Triol: 75 Mole %

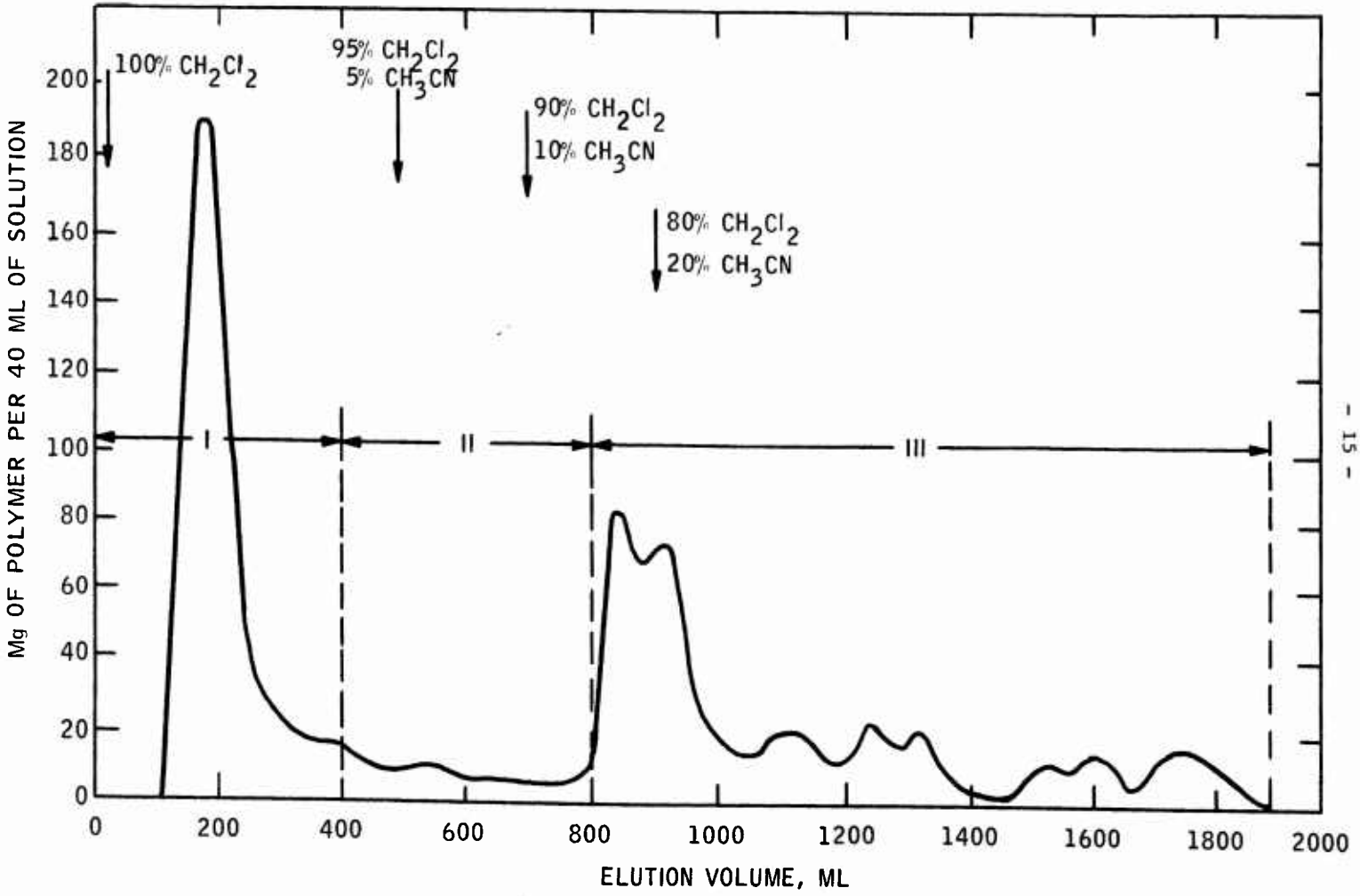

Figure 7. Elution Profile of Sinclair's R-45M, lot 805201; stepwise elution from silica gel.

2. Sinclair's R-15M

To determine whether there is a substantial difference between R-45M and R-15M, a sample of R-15M, lot 707203, was also characterized.

2.1. Functionality Determination

Based on number average molecular weight measurements by VPO and equivalent weight measurements based on the reaction of the prepolymer with p-toluenesulfonyl isocyanate the following functionality was calculated:

$$f = \frac{(Mn)o}{Eq.\ Wt} = \frac{3420}{1380} = 2.48$$

This functionality is identical to lot 805101, of the R-45M prepolymer. There is a significant, but not dramatic difference in molecular weight between the R-15M (3400) and the R-45M (2800).

2.2. Functionality Distribution Measurements

The elution schedule was identical to the one used for the R-45M prepolymer. The resulting elution profile is shown in Figure 8. Oxidative crosslinking was again in evidence when the individual cuts comprising Fraction I were combined and stripped under vacuum at 40°C and subsequently exposed to air. The initial part of the profile (see dotted line of Fraction I, Figure 8) was therefore repeated. Fraction I of the repeat fractionation accounts for 44.0 wt % of the total polymer as compared to 47.6% of the initial fractionation.

Analysis of Fraction I showed that this fraction was difunctional as had been expected. Fractions II and III were found to be trifunctional.

Complete analyses are given below:

Identification: 447-90 and 447-112
Silica gel/polymer ratio: 100/1
Polymer charged to column: 1.20 g
Total polymer recovery: 86.5%

Fraction	Wt % of Total	Equivalent Weight (Grams/mole of OH)	$\overline{(Mn)}o$	Functionality
I	47.6	----------	*	----------
	44.0**	2750	5700	2.07
II	24.1	810	2450	3.02
III	14.8	716	2180	3.04

* This fraction could not be analyzed because of oxidative crosslinking

** Repeat of initial segment of profile

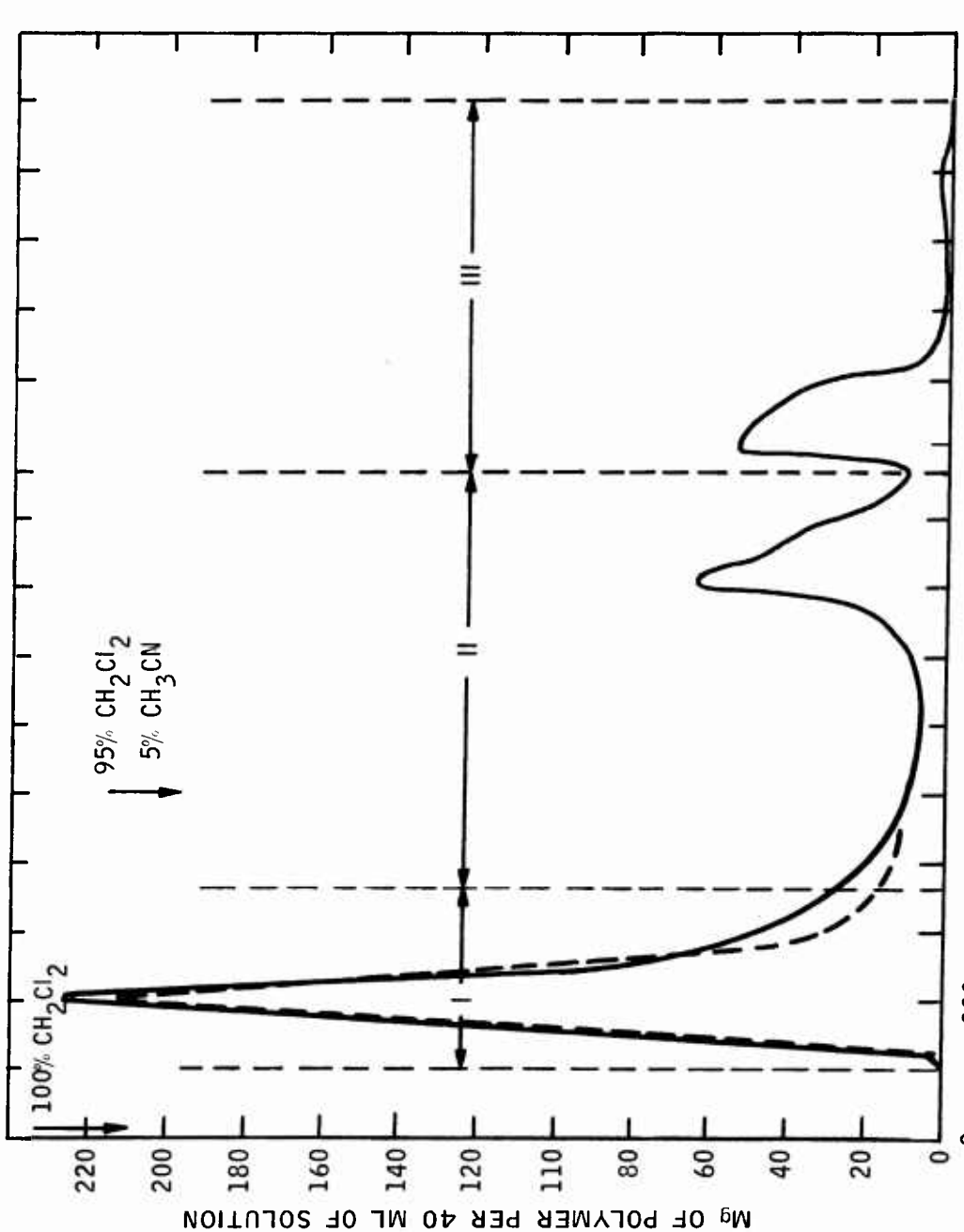

Figure 8. Elution Profile of Sinclair's R-15M, lot 707203; stepwise elution from silica gel.

Based on the above data we can conclude that about 45% of this prepolymer is difunctional, about 40 wt % is trifunctional and the remaining prepolymer (15%) which could not be desorbed is also presumed to be trifunctional.

A comparison of the functinality distribution of the R-45M and the R-15M prepolymers shows that trifunctional prepolymer is the major component (morethan 50%) in both prepolymers. The R-15M appears to have a slightly higher difunctional content than the R-45M. This apparently slight difference in difunctional polymer content may further diminish upon analysis of additional lots of R-15M.

B. Functionality and Functionality Distribution Measurements of General Tire's OH-TELAGEN Prepolymers

Samples of the low molecular weight, hydrogenated, OH-Telagen-S, had previously been characterized (1) and found to contain non-, mono- and difunctional prepolymer. We have analyzed one additional lot of OH-Telagen-S which is being used in a program on the evaluation of curing agents. A sample of the higher molecular weight, unsaturated OH-Telagen, has also been analyzed for the first time on this program. Fractionation of this prepolymer will be scaled-up to provide sufficient quantities of pure mono- and difunctional material for evaluation of mechanical properties of cured gumstocks.

1. OH-TELAGEN-S (Nominal Mn=2000), Lot 242AM 273BH

This lot of OH-Telagen-S was purchased from General Tire and Rubber Company for use on Contract FO4611-68-C-0045, "Synthesis and Evaluation of Curing Agents."

1.1. Functionality Determination

Equivalent weight measurements were made by reaction of the prepolymer with p-toluene sulfonyl isocyanate. The following results were obtained:

Equivalent Weight (Grams/mole of OH)
1230
1225
1210
1260
1225
Average: 1230 g/mole of OH

Number average molecular weights were determined by VPO in chloroform at 37°C (see Figure 9). The extrapolated molecular weight $(\bar{M}n)o$ is 1810. Based on these measurements the calculated functionality is:

$$f = \frac{1810}{1230} = 1.47$$

1.2. Functionality Distribution Measurements

The polymer was fractionated by stepwise elution from silica gel using the following solvent schedule: 100% CCl_4, mixtures of CCl_4 and CH_2Cl_2, 100% CH_2Cl_2 and mixtures of CH_2Cl_2 and CH_3CN. The elution profile is shown in Figure 10. The individual fractions were recombined into four major cuts. Total polymer recovery was 92.6%. Analyses of these fractions are summarized below:

Identification: 447-84
Silica gel/polymer ratio: 79/1
Total polymer charged: 1.27 g
Total polymer recovery: 92.6%

Fraction	Wt % Total	Equivalent Weight (Grams/mole of OH)	$(\bar{M}n)o$	Functionality
I	17.9	4525	2340	0.52
II	6.0	1730	1760	1.02
III	30.8	1010	2010	1.99
IV	37.9	770	1580	2.05
	92.6%			

Fraction I and II comprise non- and monofunctional components. They account for about 24% of the total prepolymer. The remainder (fractions III and IV) is difunctional. Fraction I is apparently a 50/50 mixture of non- and monofunctional polymer. The functionality distribution of this lot of OH-Telagen-S is therefore as follows:

- 9% nonfunctional
- 15% monofunctional
- remainder difunctional

Similar functionality distributions were found for previously analyzed lots of OH-Telagen-S.

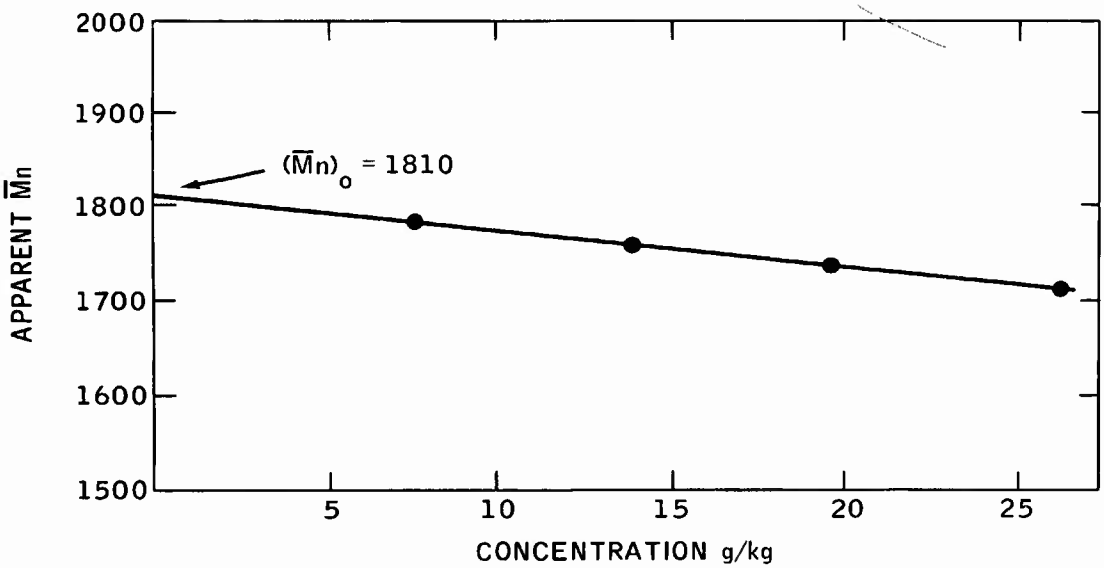

Figure 9. Concentration dependence of number average molecular weight for OH-Telagen-S, lot 242 AM 273 BH, in chloroform at 37°C.

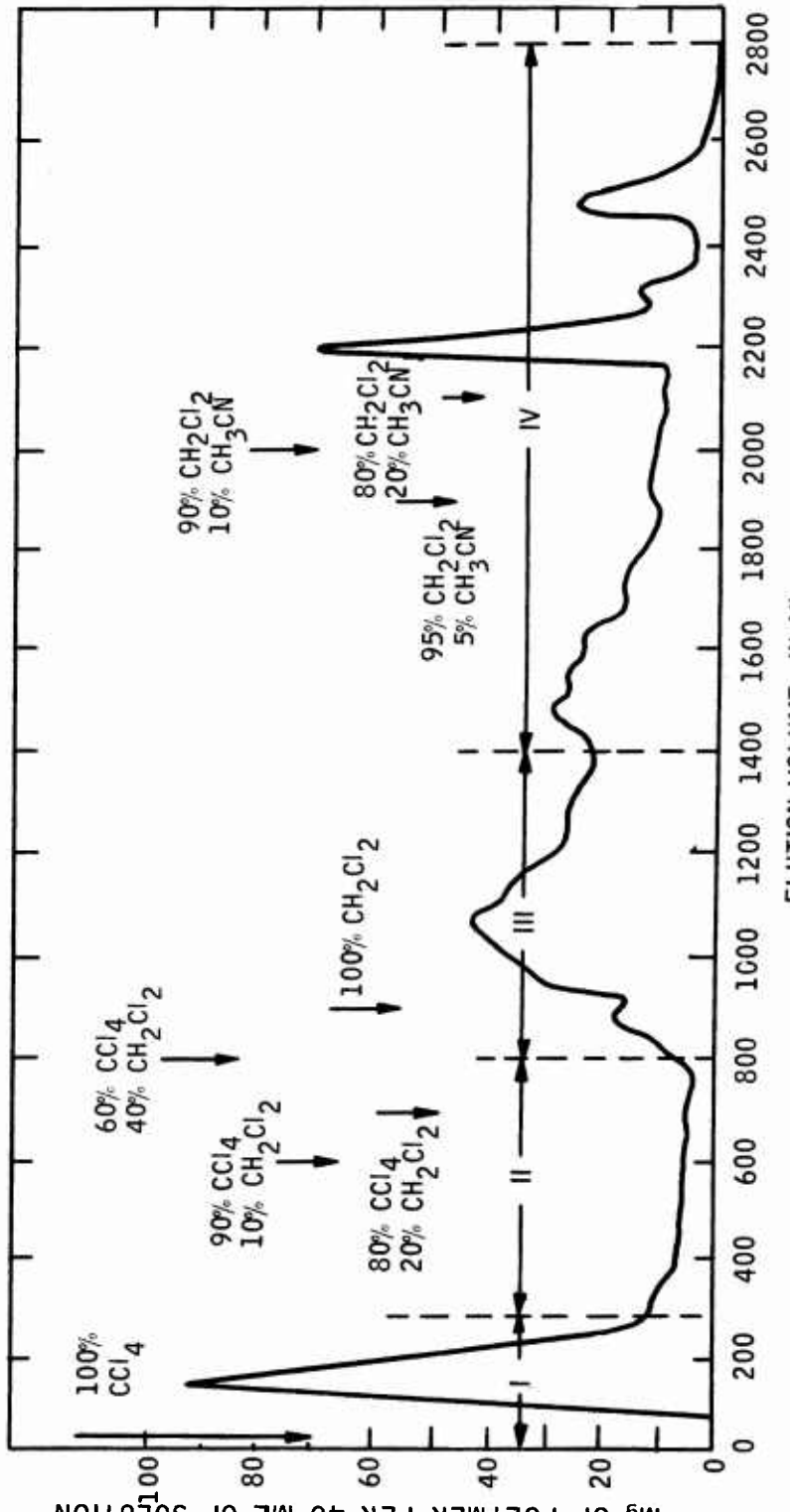

Figure 10. Elution Profile for OH-Telagen-S, lot 242 AM 273 BH; stepwise elution from silica gel.

2. OH-TELAGEN (Nominal Mn=5000), Lot 242 AM 292/316 AM6

This lot of OH-Telagen (nominal molecular weight 5000) was purchased from General Tire and Rubber Company for use on both Contracts FO4611-69-C-0046 and FO4611-68-C-0045. This polymer is the first unsaturated, hydroxyfunctional prepolymer of the Telagen series of 5000 nominal molecular weight that we have tried to fractionate by functionality. Fractionation of this prepolymer will be scaled-up for evaluation of mechanical properties of a gumstock prepared from a pure difunctional hydroxy-terminated polybutadiene prepolymer.

2.1. Functionality Determination

Number average molecular weights were determined in chloroform at 37°C (see Figure 11), yielding an extrapolated molecular weight by VPO of $(\overline{Mn})_o = 4260$.

Equivalent weight measurements based on the reaction of the prepolymer with p-toluene sulfonyl isocyanate are as follows:

Equivalent Weight (Grams/mole of OH)
3064
3015
3024

Average: 3034 g/mole of OH

Based on these measurements, the calculated functionality is:

$$f = \frac{4260}{3034} = 1.40$$

This calculated overall-functionality suggests the presence of very substantial quantities of non- and monofunctional components.

2.2. Functionality Distribution Measurements

This OH-Telagen prepolymer differs from previously characterized prepolymers of the OH-Telagen-S series in both molecular weight (4300 vs 2000) and unsaturation (OH-Telagen-S is the hydrogenated analogue of OH-Telagen). The OH-Telagen prepolymer also differs from Sinclair's R-45M, another hydroxy-functional polybutadiene: OH-Telagen is reportedly a mixture of non-, mono- and difunctional polymer whereas R-45M has been shown to be composed of di- and trifunctional prepolymer.

Our first series of experiments were concerned with the development of an optimum solvent schedule for fractionation of the polymer by stepwise elution from silica gel. Also the minimum silica gel/polymer ratio required to give satisfactory separation of mono- and difunctional prepolymer must be defined. This ratio will determine column size and the amount of prepolymer that can be processed upon scale-up.

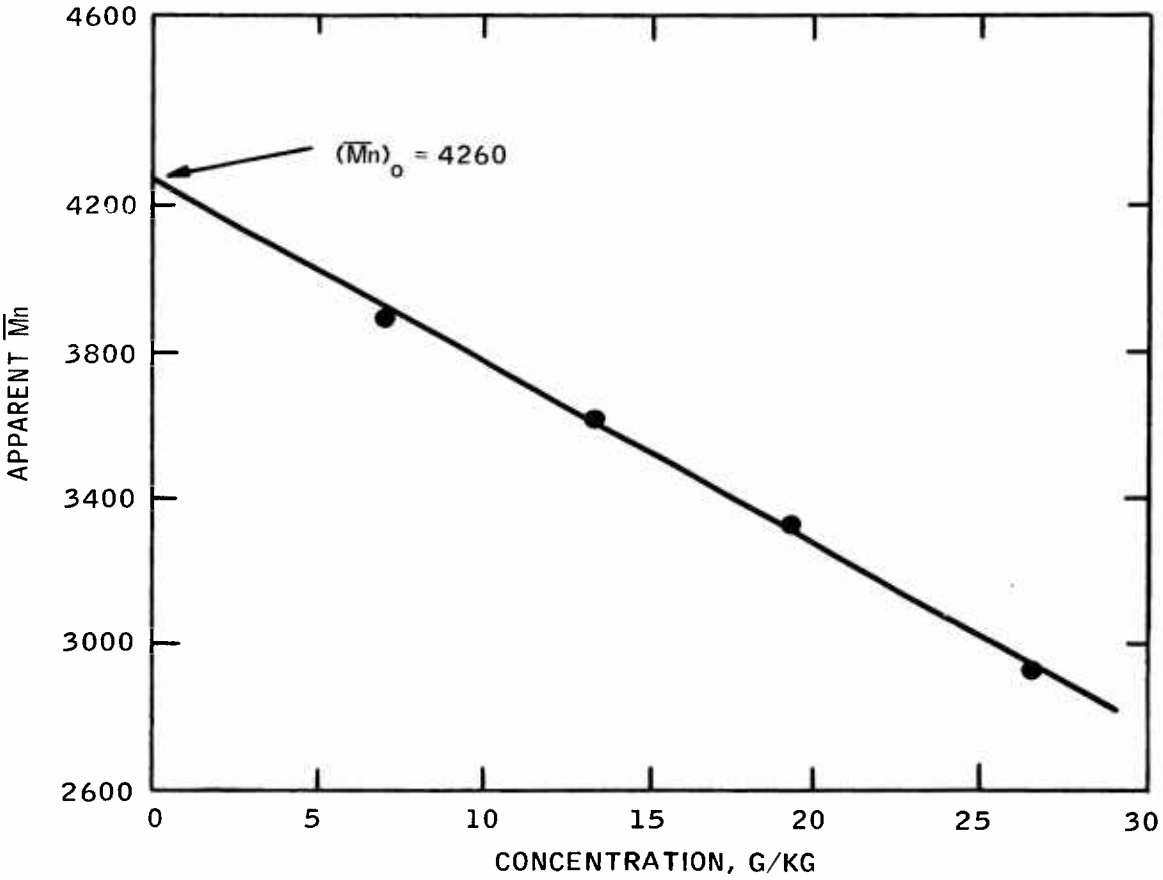

Figure 11. Concentration dependence of number average molecular weight by VPO for OH-Telagen, lot 242 AM 292/316 AM6, in chloroform at 37°C.

The first fractionation study was carried out at a silica gel/polymer ratio of 95/1 using CCl_4 and mixtures of CCl_4 and $CHCl_3$ of progressively higher $CHCl_3$ content. The resulting elution profile is shown in Figure 12. It is apparent from this profile that no significant amount of polymer was eluted from the column in response to CCl_4. The first significant elution (fraction II) was in response to mixtures of $CCl_4/CHCl_3$ and/or 100% $CHCl_3$. Fraction II was followed immediately by the major fraction (major peak of fraction III) in response to 100% $CHCl_3$. The fractionation was terminated after 83.6% of the polymer had been recovered. Analyses of the fractions shows some separation by functionality. Fraction III apparently contained some monofunctional material in addition to the difunctional polymer.

Identification: 447-116
Silica gel/polymer ratio: 95/1
Total polymer charged: 1.372g
Total polymer recovery: 83.6%

Fraction	Wt % Total	Equivalent Weight (Grams/mole of OH)	$(\overline{Mn})_o$	Functionality
I	0.4	---------- *	----------	
II	16.4	6000	4800	0.80
III	66.8	2600	4540	1.75
	83.6			

* Analysis could not be obtained because of small sample size.

The profile indicated that CCl_4 lacked sufficient desorbing action whereas $CHCl_3$ was too strong a desorbing agent to permit separation by functionality. To confirm the strong desorbing power of $CHCl_3$, a fractionation study was carried out using only $CHCl_3$ as the eluting solvent. The resulting profile is depicted in Figure 13. The profile very clearly demonstrates the desorbing action of $CHCl_3$ and the lack of separation of the polymer into distinct peaks. Elution from the column was terminated after 81.2% recovery.

Specific conditions are summarized below:

Identification: 447-134
Silica gel/polymer ratio: 100/1
Total polymer charged: 0.956g
Total polymer recovery: 81.2%

No analyses were carried out.

On the basis of these two experiments, it was concluded that CCl_4 should be used as the initial solvent to allow adsorption of the polymer on the silica gel. It was further hoped that a suitable mixture of CCl_4 and $CHCl_3$ should give adequate separation of the polymer by functionality. It was also apparent that the silica gel/polymer ratio could be significantly reduced from the current level of 100/1.

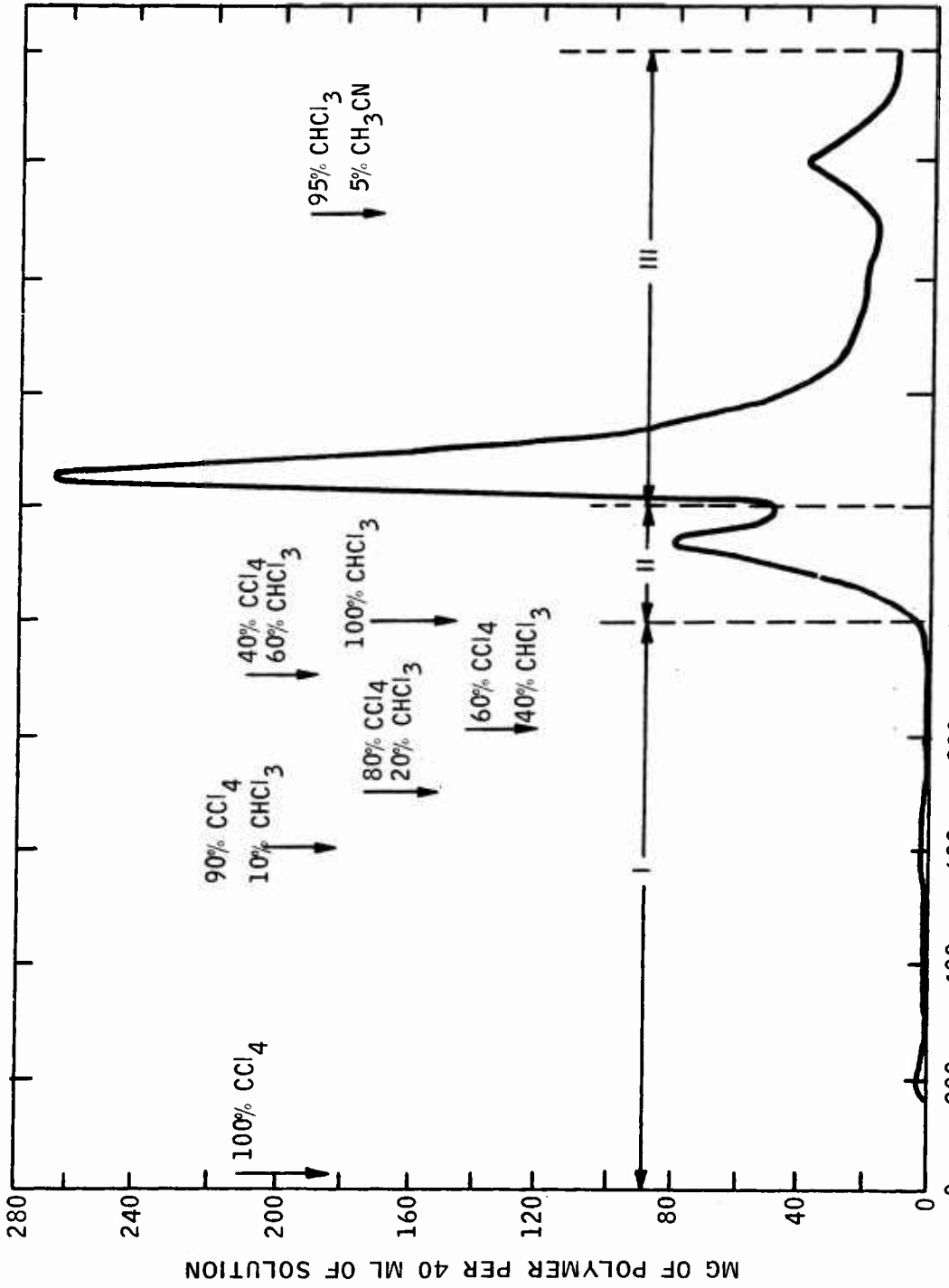

Figure 12. Elution profile for OH-Telagen, lot 242 AM 292/316 AM6 by stepwise elution from silica gel. Run: 447-116; silica gel/polymer ratio = 95/1.

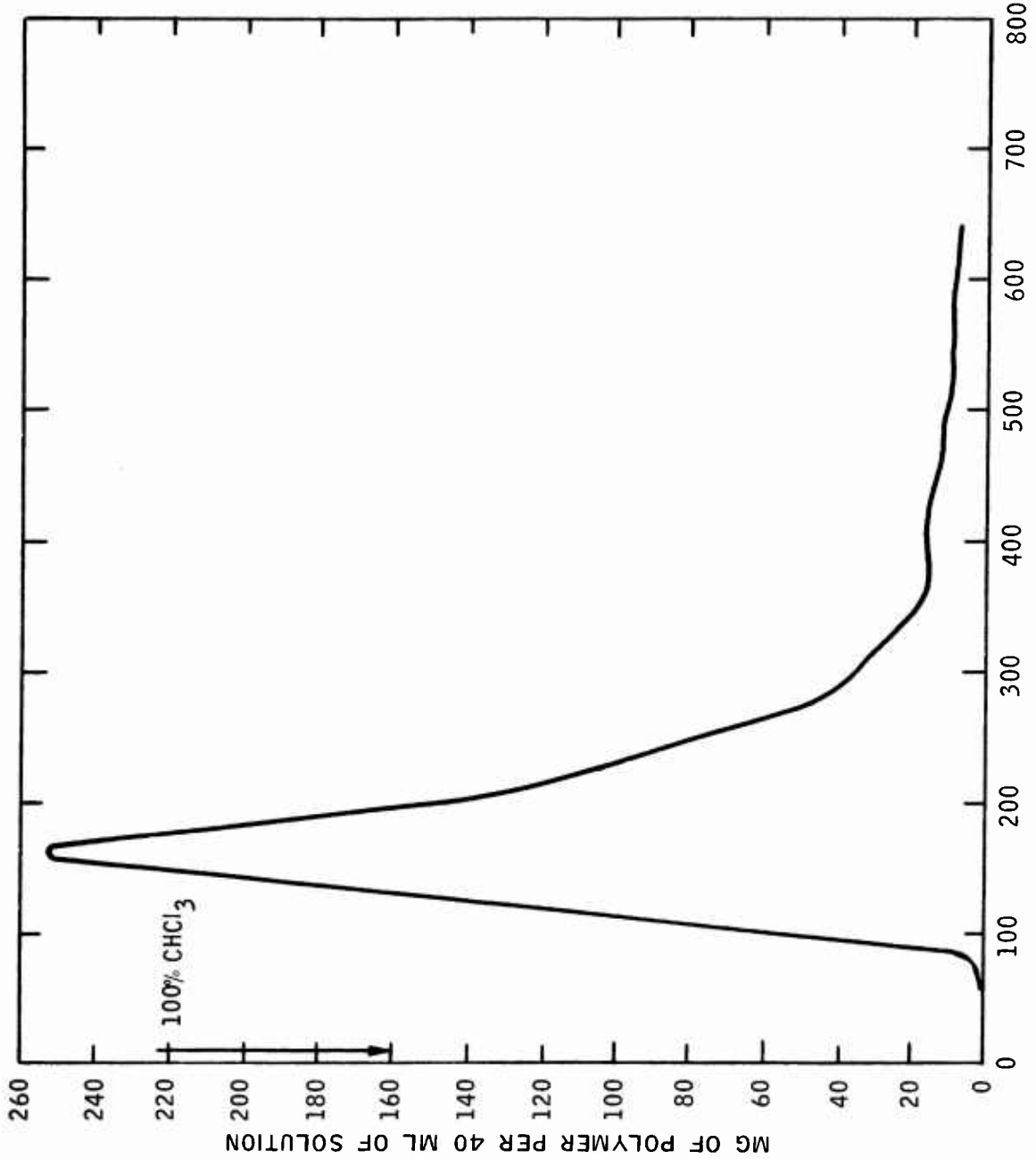

Figure 13. Elution profile for OH-Telagen, lot 242 AM 292/316 AM6 by stepwise elution from silica gel. Run: 447-134; silica gel/polymer ratio: 100/1

In subsequent studies, we lowered the silica gel/polymer ratio and also investigated the effect of the chloroform content of the carbon tetrachloride/chloroform solvent mixture on the efficiency of polymer fractionation. Figure 14 shows the elution profile at a silica gel/polymer ratio of 26/1. Even at this considerably lower ratio, less than 1% of the polymer is eluted by CCl_4 and $CCl_4/CHCl_3$ mixtures containing up to 20% chloroform. There is a significant response to the 60/40 $CCl_4/CHCl_3$ solvent mixture which elutes about 26% (Fraction II) of the total polymer from the column. The bulk of the polymer is subsequently eluted in response to 100% chloroform. Fractionation was terminated after 89.1% of the polymer had been recovered. Analyses of the fractions are summarized below:

Identification: 447-138
Silica gel/polymer ratio: 26/1
Total polymer charged: 3.869 g
Total polymer recovery: 89.1%

Fraction	Wt %	Equivalent Weight (Grams/mole of OH)	$(\bar{M}n)o$	Functionality
I	0.9	---------- *	----------	----------
II	25.9	5800	4900	0.84
III	10.3	3140	4700	1.50
IV	52.0	2620	5200	1.98
	89.1			

* No analysis could be obtained because of the small sample size.

Based on these data the total non- and monofunctional prepolymer content is in excess of 27% (total of I and II). Fraction III is approximately a 50/50 mixture of mono- and difunctional prepolymer. The total non- and monofunctional content is therefore about 32%.

Further fractionation studies with the OH-Telagen prepolymer are being carried out at further reduced silica gel/polymer ratios. Figure 15 shows the elution profile at a gel/polymer ratio of 15.6/1 using 100% CCl_4, 70/30 $CCl_4/CHCl_3$ and 100% $CHCl_3$ in succession. By eliminating $CCl_4/CHCl_3$ mixtures of 95/5, 90/10 and 80/20 the elution profile was considerably condensed. The first major peak (Fraction II) again accounts for 25% of the total polymer. Analyses are summarized in the following table.

Identification: 447-160
Silica gel/polymer ratio: 15.6/1
Polymer charged to column: 6.415 g
Total Polymer recovery: 92.1%

Fraction	Wt. %	Equivalent Weight (Grams/Mole of OH)	$(\bar{M}n)_o$	Functionality
I	0.3	---------- *	----------	----------
II	24.7	4540	4700	1.04
III	10.5	4790	4900	1.02
IV	56.6	2620	5000	1.91
	92.1%			

* Sample too small for analysis

These data confirm in essence the functionality distribution measurements obtained in run 447-138. It appears that some difunctional prepolymer may have been included in fraction II as a result of the reduced silica gel/polymer ratio. The total of non- and monofunctional components is therefore somewhat less than the combined total of fractions I, II and III (less than 35%).

We believe that the silica gel/polymer ratio can be further reduced by adjusting the desorbing power of the solvents. These factors are being explored to define optimum condition for scale-up of the chromatographic separation of the OH-Telagen prepolymer into its functional components.

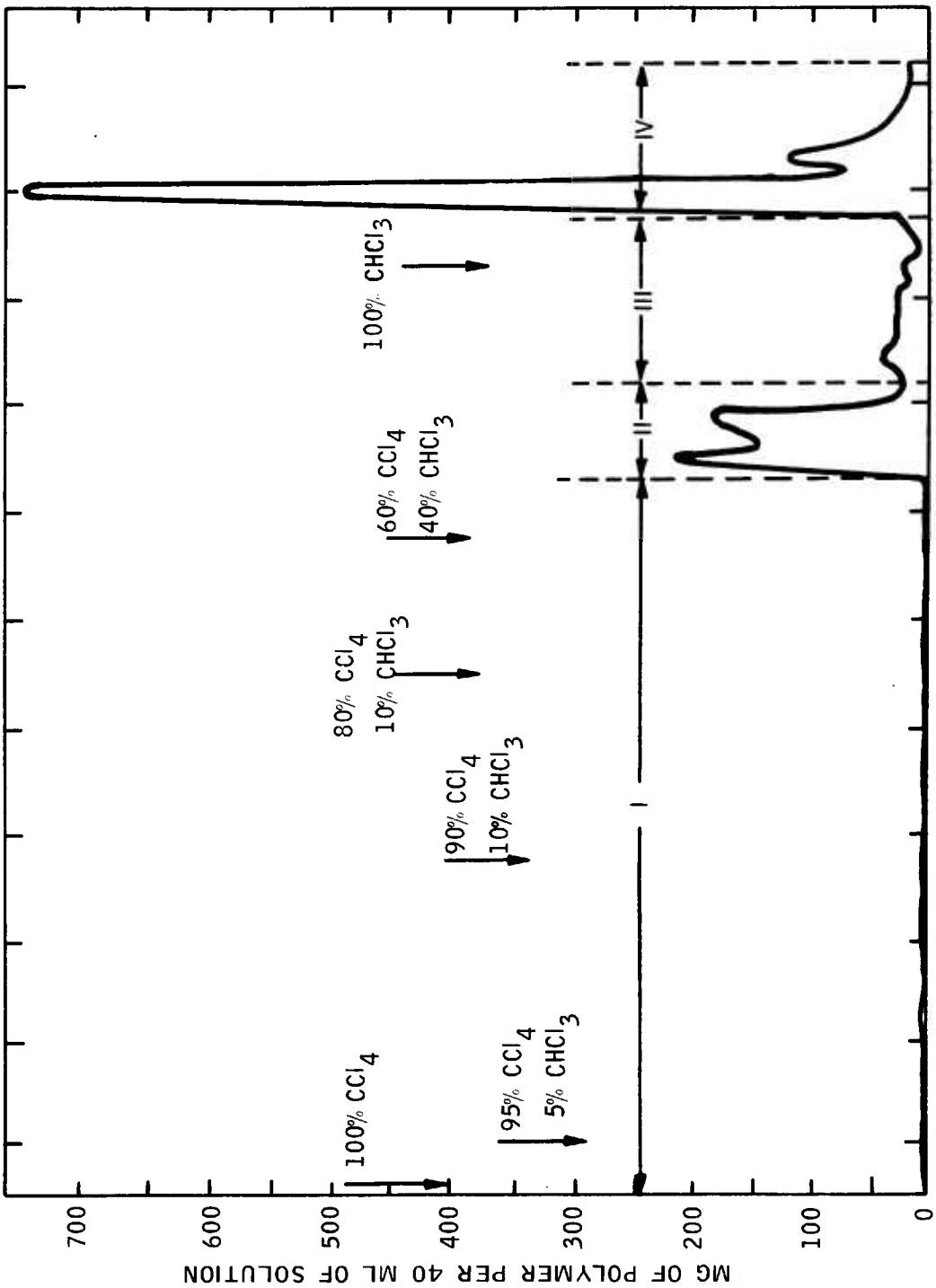

Figure 14. Elution profile for OH-Telagen, lot 242 AM 292/316 AM 6; stepwise elution from silica gel. Run: 447-138; silica gel/polymer ratio = 26/1.

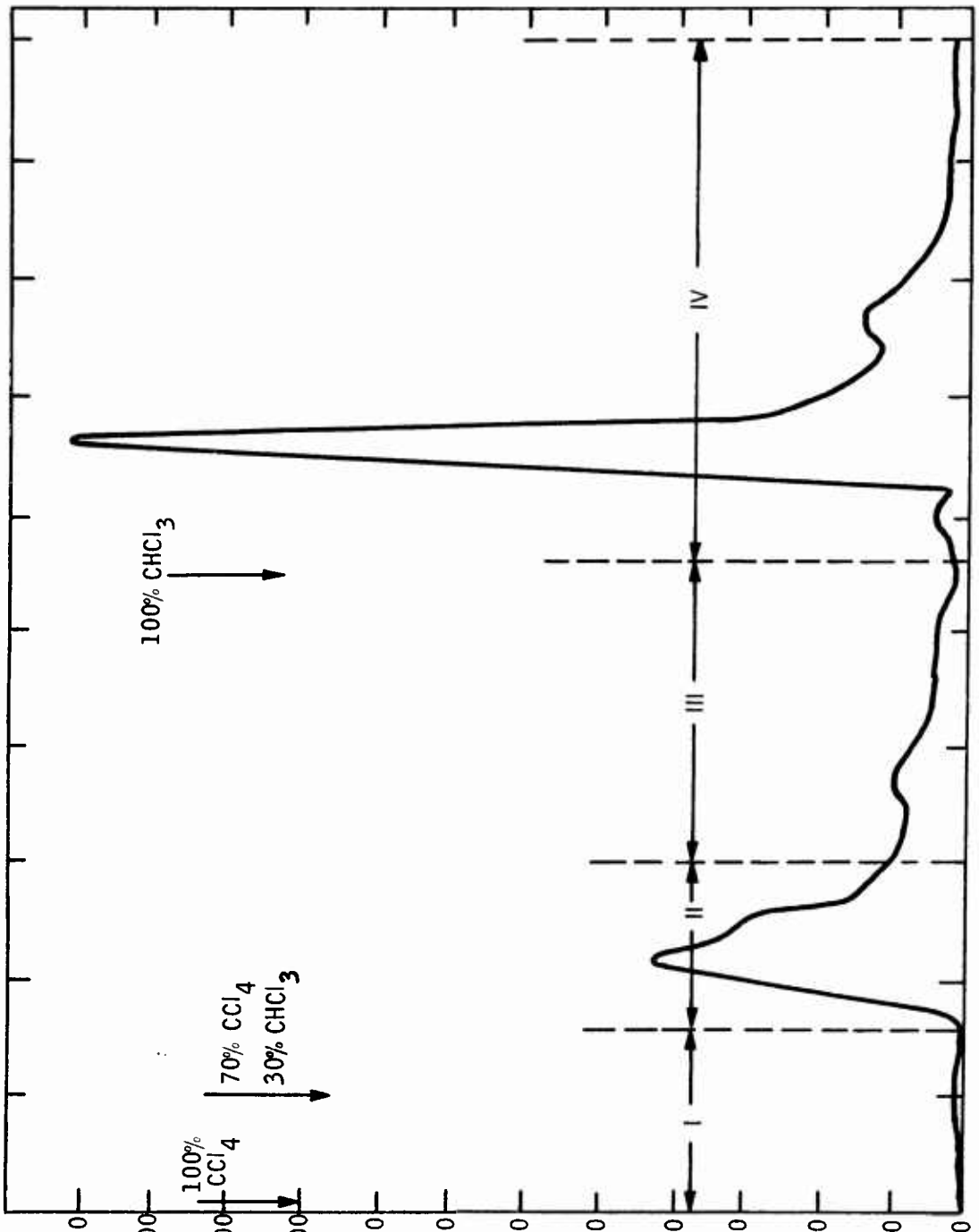

Figure 15. Elution profile for OH-Telagen, lot 242 AM 292/316 AM6 by stepwise elution from silica gel.
Run: 447-160, silica gel/polymer ratio = 15.6/1.

C. Functionality and Functionality Distribution Measurements of General Tire's COOH-TELAGEN

General Tire and Rubber Company produces also the carboxy analogue of the OH-Telagen prepolymer series. Again both a hydrogenated, COOH-Telagen-S, and the unsaturated analogue, COOH-Telagen are available. Samples of both prepolymers were analyzed on this program.

1. COOH-TELAGEN-S (Nominal 2000), Lot 242AM 273CHR

Previous lots (1) of COOH-Telagen-S prepolymer which had been analyzed had varied in total non- and monofunctional polymer content from 18 to 38%, the bulk of this fraction being monofunctional. This latest lot of COOH-Telagen-S had a non- and monofunctional prepolymer content of 25%.

1.1. Functionality Determination

This prepolymer lot was found to contain about 0.45% volatiles. Molecular weights were obtained after removal of the volatile components. The concentration dependence of apparent molecular weight by VPO in chloroform at 37°C is shown in Figure 16. Of particular interest is the positive slope of the molecular weight dependence on concentration, the molecular weight decreasing with decrease in polymer concentration. This reflects at least in part the association of the prepolymer through its carboxy-functional groups. None of the OH-prepolymers show this type of concentration dependence. The extrapolated molecular weight, $(Mn)_o$=2220. The equivalent weight of this prepolymer was determined by potentionmetric titration of an MEK solution of the polymer with 0.1 N tetrabutyl ammonium hydroxide in methanol yielding a value of 1170 g/mole of COOH.

Based on these measurements, the calculated functionality is:

$$f = \frac{2220}{1170} = 1.89$$

1.2. Functionality Distribution Measurements

To determine its functionality distribution the polymer was fractionated on silica gel using the following solvent schedule: 100% CCl_4, mixtures of CCl_4 and $CHCl_3$, 100% $CHCl_3$ and mixtures of $CHCl_3$ and CH_3CH_2OH. The resulting elution profile is shown in Figure 17 Analyses of the recombined fractions are summarized below:

Identification: 447-41
Silica gel/polymer ratio: 96/1
Polymer charged to column: 1.57g
Total Polymer Recovery: 91.9%

Fraction	Wt % of Total	Equivalent Weight (Grams/mole COOH)	$(\bar{M}n)_o$	Functionality
I	6.6	7100	2300	0.32
II	18.1	2830	2800	0.99
III	62.7	1060	2150	2.03
IV	4.5	1050	2120	2.02
	91.9			

The first fraction accounting for 6.6 wt % is a mixture of non- and monofunctional prepolymer. Based on its overall functionality of 0.32, approximately 1/3 is nonfunctional (2.2%) and 2/3 is monofunctional (4.4%). Fraction II (18.1%) is clearly monofunctional and fractions III and IV are difunctional. The residual 8% which could not be desorbed are presumably also difunctional. The functionality distribution of this prepolymer is therefore as follows:

Nonfunctional: 2.2%
Monofunctional: 4.4 + 18.1 $\simeq$ 22-23%
Difunctional: $>$67%

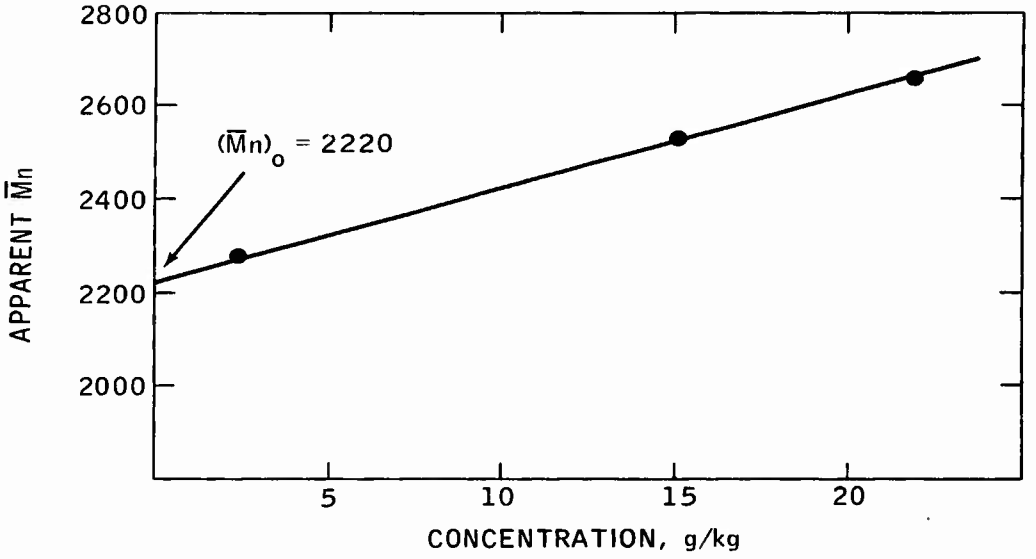

Figure 16 Concentration dependence of molecular weight for COOH-Telagen-S, batch no. 242 AM 273 CHR by VPO in chloroform at 37°C.

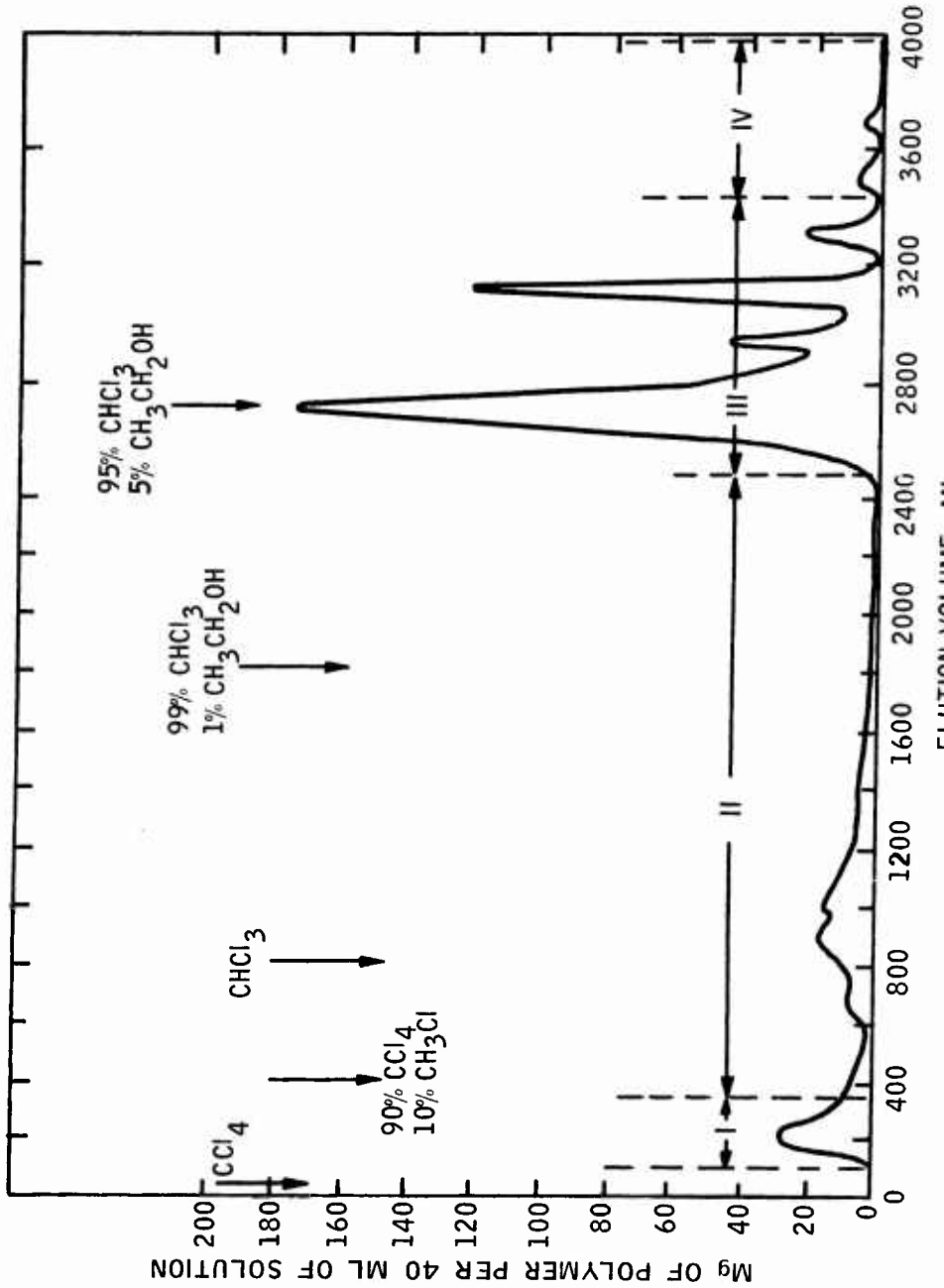

Figure 17. Elution Profile for COOH-Telagen-S, Batch No. 242AM 273 CHR, by Stepwise Elution from Silica Gel. Run 447-41 silica gel/polymer ratio = 96/1.

2. COOH-TELAGEN (Nominal 5000), Lot 126

This prepolymer is also being used on the curative program for evaluation of aziridine curing agents. It is the carboxy-functional analogue of the OH-Telagen discussed in Section B2.

2.1. Functionality Determination

Number average molecular weight measurements by VPO in chloroform at 37°C yielded an extrapolated molecular weight of $(Mn)o = 4400$ (see Figure 18).

The equivalent weight of the prepolymer was determined by potentiometric titration of an MEK solution of the polymer with 0.1 N tetrabutyl ammonium hydroxide in methanol yielding a value of 2650 g/mole of COOH.

Based on these measurements, the calculated functionality is:

$$f = \frac{4400}{2650} = 1.66$$

2.2. Functionality Distribution Measurements

In our first fractionation study with the COOH-Telagen prepolymer we employed the same solvent schedule that had previously been applied successfully to the lower molecular weight (2300), hydrogenated prepolymer, COOH-Telagen-S. Polymer recovery in excess of 95% had been realized with the COOH-Telagen-S. The unsaturated, higher molecular weight COOH-Telagen, however, upon fractionation gave only 50% recovery.

Figure 19 shows the resulting elution profile after the particular solvent schedule used. Fraction I could not be analyzed because of the small quantity involved. The infrared spectrum, however, showed a weak COOH absorption band. Since the following fraction was found to be composed of non- and monofunctional polymer, Fraction I is also believed to be a mixture of non- and monofunctional material. Inspection of individual cuts comprising Fraction II revealed the presence of a crystalline material which is believed to be additive (antioxidant). These cuts were not included in Fraction II but are reflected in the total percentage of Fraction II. Analyses of the fractions showed that Fraction II is a mixture of non- and monofunctional material whereas Fraction III is purely monofunctional. Fraction IV was essentially difunctional. The remaining 49% which could not be desorbed are also believed to be difunctional. The total non- and monofunctional content is therefore about 27%. The results of the fractionation are summarized on the following page.

Identification: 447-114
Silica gel/polymer ratio: 100/1
Total polymer charged: 1.302 g
Total polymer recovery: 51.4%

Fraction	Wt %	Equivalent Weight (Grams/Mole of COOH)	$(\bar{M}n)o$	Functionality
I	2.3	---------- * ----------		
II	18.6	6720	5100	0.76
III	5.7	3810	3800	1.0
IV	24.8	1950	3800	1.95
	51.4			

* Because of small sample size no analysis could be obtained.

In attempts to improve polymer recovery, 100% $CHCl_3$ was used as the initial solvent. Figure 20 depicts the elution profile using 100% $CHCl_3$ and subsequently 95/5 $CHCl_3/CH_3CH_2OH$. Although polymer recovery was somewhat improved (68.8% vs 51.4%) separation efficiency was adversely affected. Fraction I (33%) was a mixutre of non-, mono- and difunctional polymer. Fraction II was a mixture of mono- and difunctional polymer and Fraction III was difunctional. Results of fractionation 447-146 are summarized below.

Identification: 447-146
Silica gel/polymer ratio: 100/1
Total polymer charged: 1.338 g
Total polymer recovery: 68.8%

Fraction	Wt %	Equivalent Weight (Grams/Mole of COOH)	$(\bar{M}n)o$	Functionality
I	33.0	6200	5300	0.85
II	21.2	2380	3800	1.60
III	14.6	2000	4100	2.05
	68.8			

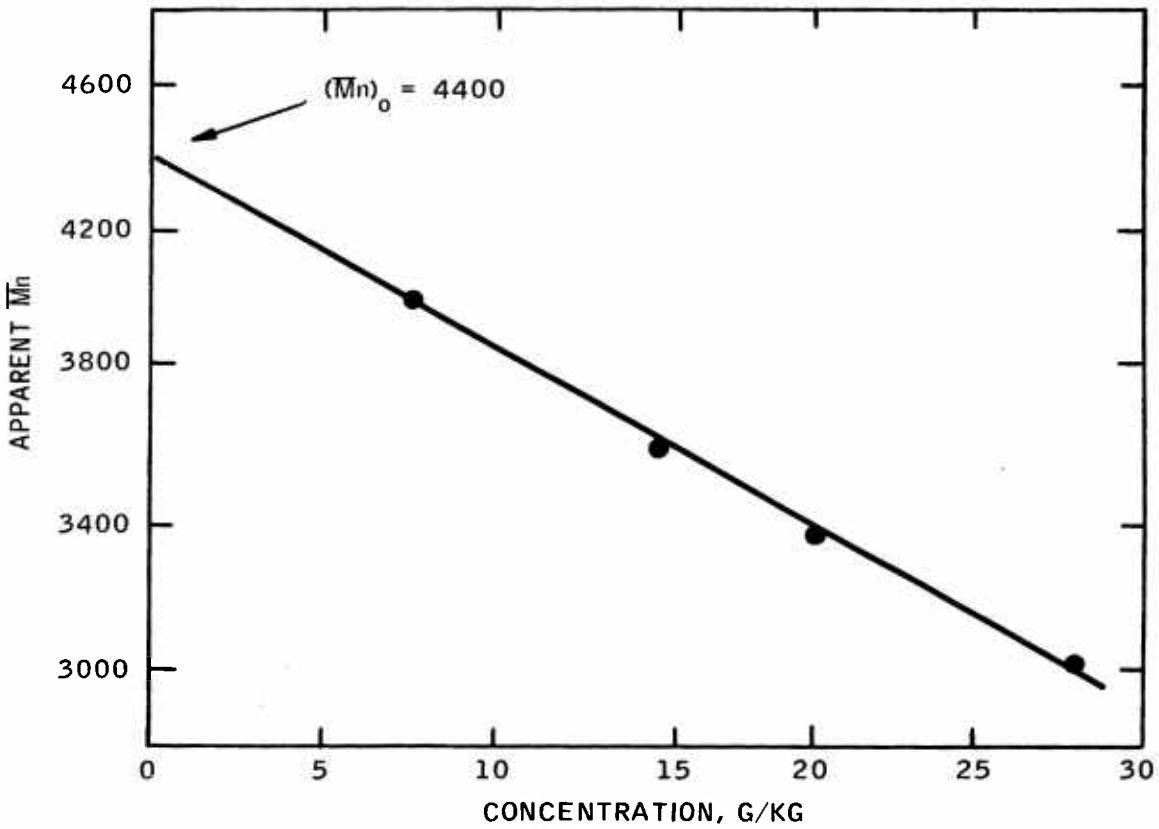

Figure 18. Concentration dependence of number average molecular weight by VPO for COOH-Telagen, lot 126, by VPO in chloroform at 37°C.

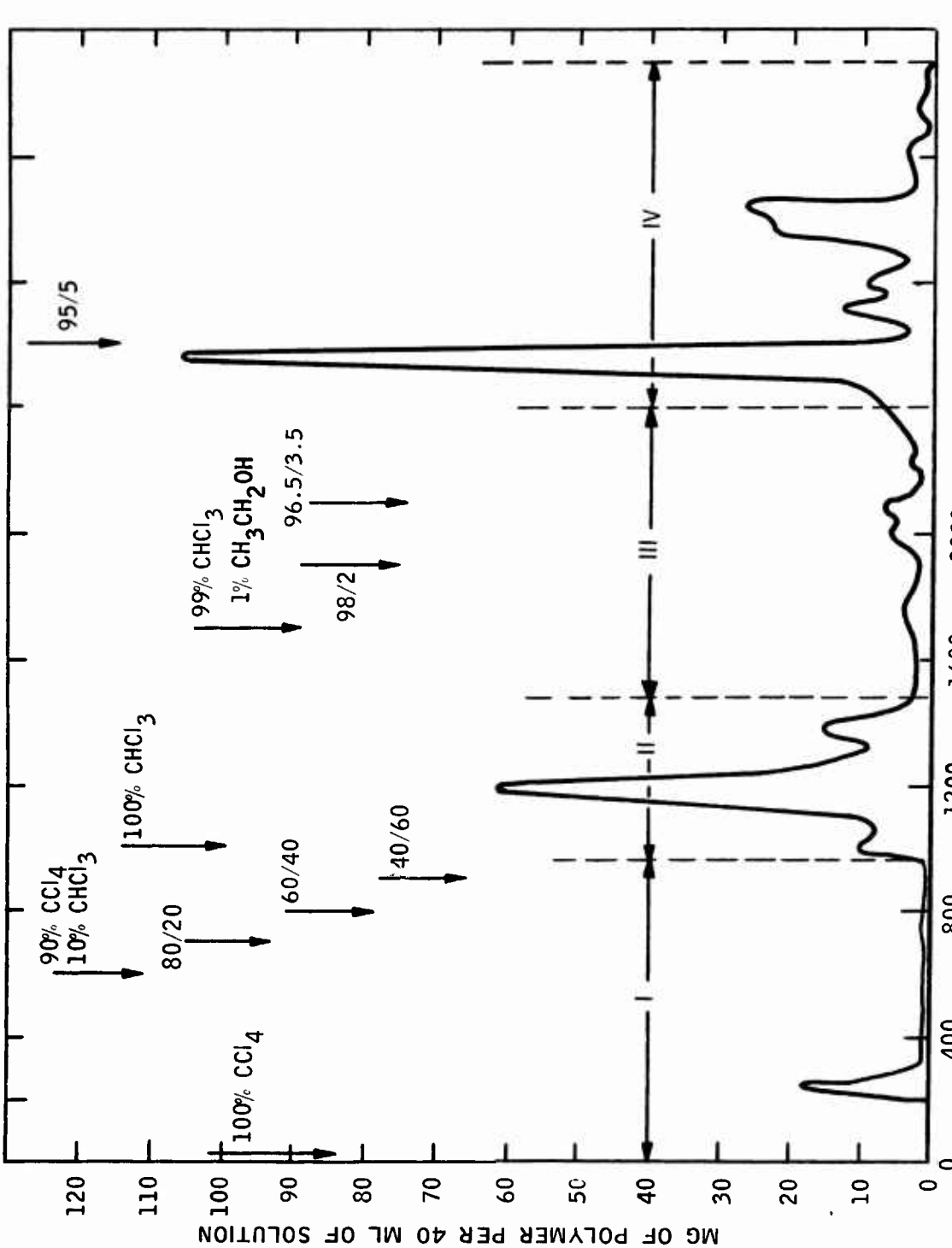

Figure 19. Elution profile for COOH-Telagen, lot 126 by stepwise elution from silica gel. Run: 447-114; silica gel/polymer ratio = 100/1

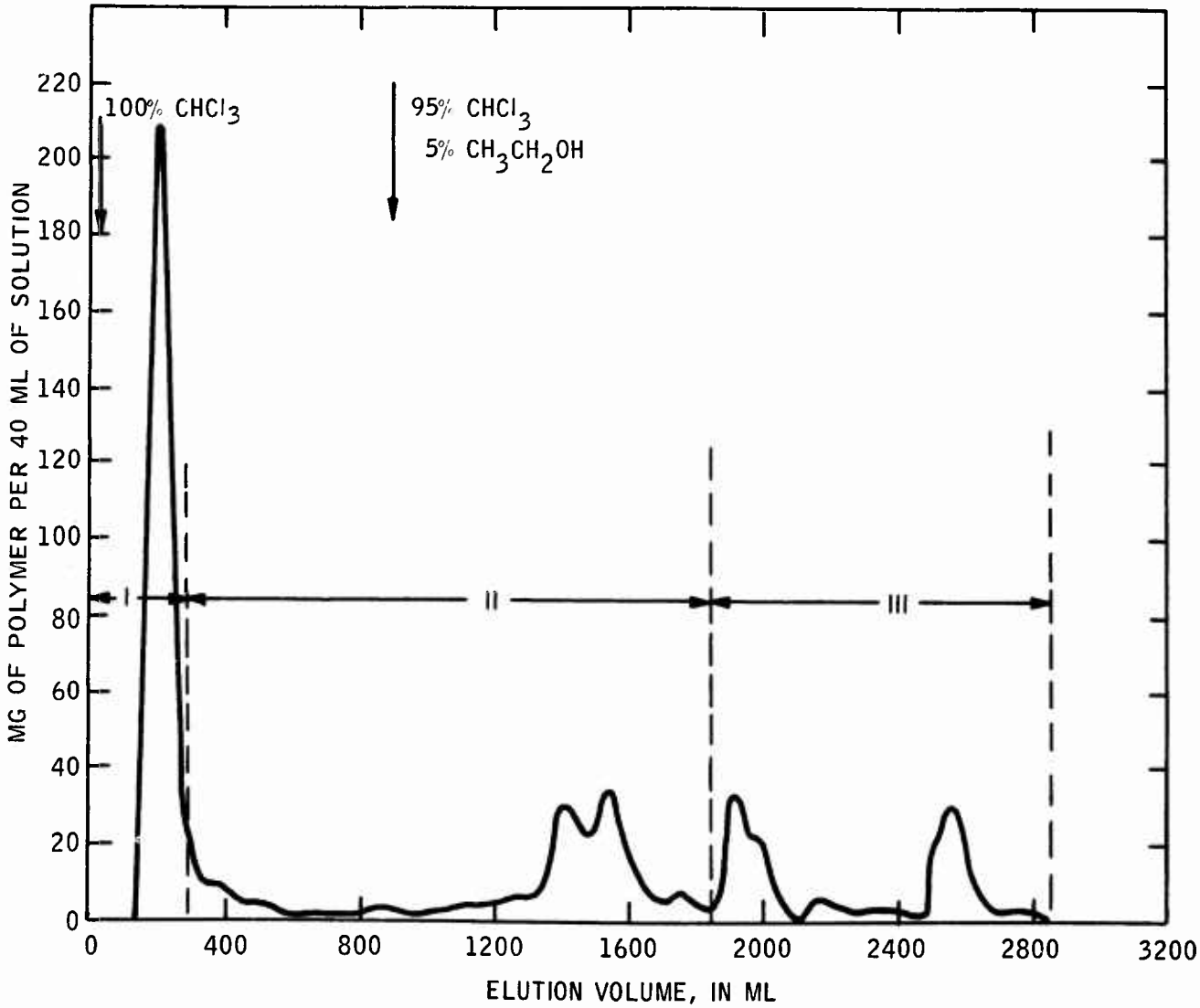

Figure 20. Elution profile for COOH-Telagen, lot 126 by stepwise elution from silica gel. Run: 447-146; silica gel/polymer ratio = 100/1

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13. ABSTRACT

Functionality and functionality distribution measurements have been carried out on six different polybutadiene prepolymers containing hydroxy or carboxy functionality which are currently of interest to the Air Force. The specific prepolymers are: Sinclair's Poly B-D R-45M and R-15M, hydroxy-functional butadiene homopolymers prepared by free radical polymerization and General Tire's Telagen prepolymer series, prepared by anionic polymerization. The Telagen prepolymer series comprises the following polymers: the OH-Telagen (nominal Mn=5000) and its low molecular weight (Mn=2000), saturated counterpart, OH-Telagen-S, and the corresponding carboxy-functional analogues, COOH-Telagen and COOH-Telagen-S.

Number average molecular weight measurements of three different lots of the R-45M prepolymer showed little batch to batch variation. Functionality distribution measurements were obtained by elution chromatography on activated silica gel. The difunctional content was found to be approximately 40 wt % with a nominal molecular weight of 4000, the remainder (60 wt %) being trifunctional with a nominal molecular weight of 2000. All three lots of the R-45M have consistently shown this dependence of functionality on molecular weight. On a molar basis the functionality distribution of the R-45M prepolymer reflects an even high triol content: 25 mole % diol and 75 mole % triol. The functionality

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13. Abstract (Cont'd)

distribution of the R-15M was found to be similar to that of the R-45M, containing more than 50 wt % triol. In contrast to Sinclair's R-45M and R-15M prepolymers which are composed of di- and trifunctional components, the Telagen prepolymers contain non-, mono- and difunctional prepolymers. The total non- and monofunctional content of the four Telagen prepolymers which were analyzed varied from 24 to 32 wt %, the bulk of which is monofunctional.

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Number Average Molecular Weight Determination						
Equivalent Weight Determination						
Functionality						
Functionality Distribution Measurements						
Prepolymers						
Binders						
Elution Chromatography						
Sinclair's Poly B-D, R-45M and R-15M Prepolymer						
OH-Telagen						
OH-Telagen-S						
COOH-Telagen						
COOH-Telagen-S						

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